Catalytic Ozonation of Effluents from the Textile Industry

(Ozonização Catalítica de Efluentes da Indústria Têxtil)

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Dissertation presented for the Ph.D. Degree in
Chemical and Biological Engineering at the
Faculty of Engineering, University of Porto, Portugal

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June 2008

Agradecimentos

Aos meus orientadores, Prof. M. Fernando R. Pereira e Prof. José J. M. Órfão, em parte responsáveis pelo interesse que desenvolvi pela investigação científica, quero agradecer todo o apoio, motivação e enorme disponibilidade demonstrada ao longo destes anos em que trabalhámos juntos. Agradeço todas as sugestões, as críticas, os elogios e o incentivo para fazer sempre mais e melhor. Ao Prof. Órfão agradeço particularmente a paciência e a ajuda incansável que me deu nos últimos dias de escrita da tese.

Este trabalho foi financiado pela Fundação para a Ciência e a Tecnologia (FCT) (Projecto POCTI/1181 e bolsa de doutoramento SFRH/BD/18169/2004) e pela Agência de Inovação (AdI) (Projecto Anoxitrata).

Ao Laboratório de Catálise e Materiais (LCM), na pessoa do seu Coordenador Científico, Professor José Luís Figueiredo, agradeço todas as facilidades concedidas para a realização deste trabalho, nomeadamente o acesso aos equipamentos disponíveis.

Fico reconhecida ao Departamento de Engenharia Química da FEUP pela disponibilização de alguns dos respectivos serviços e laboratórios. Em particular, agradeço ao Doutor Rui Boaventura o acesso aos meios técnicos do Laboratório de Ciências do Ambiente.

Ao Doutor Carlos Moreira de Sá, Director do Centro de Materiais da Universidade do Porto (CEMUP), agradeço o apoio prestado no tratamento e interpretação dos resultados de XPS.

Ao Centro Tecnológico das Indústrias Têxtil e do Vestuário de Portugal (CITEVE), em particular ao Eng. Renato Dias, agradeço a disponibilização dos efluentes usados neste trabalho.

À Elodie agradeço a ajuda imprescindível na redacção do résumé.

Quero agradecer a todos os que passaram pelo LCM durante este período da minha vida e que, de algum modo, não me foram indiferentes. Em particular, à Cláudia, à Filomena, à Salomé, à Vera e ao Adrián, que se juntou mais recentemente ao grupo, agradeço de uma forma muito especial a amizade, o companheirismo, a ajuda, as conversas, os desabafos, e todos os bons momentos que passámos juntos.

E porque há vida para além do doutoramento, agradeço a todos os meus amigos por estarem sempre presentes.

Embora a minha família saiba que estou eternamente grata por tudo o que fazem por mim, não poderia deixar de citar a minha Mãe, o meu Pai e o meu irmão, o Nuno, que certamente se orgulham de me verem chegar ao fim desta etapa. Está na hora de mostrar que sei fazer algo mais do que estudar.

Finalmente, ao Paulo, a pessoa com quem eu partilho tudo (o que inclui os melhores e os piores momentos) quero agradecer o amor, o apoio incondicional, a visão optimista da vida e por fazer de mim uma pessoa melhor.

Preface

This PhD thesis was carried out at Laboratório de Catálise e Materiais (LCM), Laboratório Associado LSRE/LCM, at the Department of Chemical Engineering, Faculty of Engineering of the University of Porto.

The thesis is divided in six parts. Parts I and VI correspond to the introduction and main conclusions, respectively. The main core of the text (Parts II, III, IV and V) is structurally based on 9 scientific papers, 6 of which already published (June 2008) in refereed journals, whilst the other are under review (2) or in the last phase of preparation to be submitted for publication (1).

List of publications:

Part II

P.C.C. Faria, J.J.M. Órfão, M.F.R. Pereira, *Ozone decomposition in water catalyzed by activated carbon: Influence of chemical and textural properties*. Ind Eng Chem Res **45** (2006) 2715-2721.

Part III

P.C.C. Faria, J.J.M. Órfão, J.L. Figueiredo, M.F.R. Pereira, *Adsorption of aromatic compounds from the biodegradation of azo dyes on activated carbon.* Appl Surf Sci **254** (2008) 3497-3503.

P.C.C. Faria, J.J.M. Órfão, M.F.R. Pereira, *Ozonation of aniline promoted by activated carbon*. Chemosphere **67** (2007) 809-815.

P.C.C. Faria, J.J.M. Órfão, M.F.R. Pereira, *Activated carbon catalytic ozonation of oxamic and oxalic acids*. Appl Catal B-Environ **79** (2008) 237-243.

P.C.C. Faria, J.J.M. Órfão, M.F.R. Pereira, *Catalytic ozonation of sulfonated aromatic compounds in the presence of activated carbon*. Appl Catal B-Environ **83** (2008) 150-159.

Part IV

P.C.C. Faria, D.C.M. Monteiro, J.J.M. Órfão, M.F.R. Pereira, *Metal oxides as catalysts for the ozonation of selected organic compounds*, submitted (2008).

P.C.C. Faria, J.J.M. Órfão, M.F.R. Pereira, *A novel ceria-activated carbon composite for the catalytic ozonation of carboxylic acids*. Catal Commun **9** (2008) 2121-212.

P.C.C. Faria, J.J.M. Órfão, M.F.R. Pereira, *Mineralization of aromatic substituted compounds by ozonation catalysed by ceria and a ceria-activated carbon composite,* submitted (2008).

Part V

P.C.C. Faria, J.J.M. Órfão, M.F.R. Pereira, *Activated carbon and ceria catalysts applied to the catalytic ozonation of dyes and textile effluents,* to be submitted (2008).

Abstract

Catalytic ozonation is considered an emerging powerful technology for the elimination of persistent organic compounds in water and wastewater. From a practical application point of view, the integration of such processes with aerobic or anaerobic biological processes would be of great interest for a thorough treatment of liquid effluents, such as those from the textile industry. The main goal of this thesis was to assess the suitability of selected catalytic ozonation systems for the depuration of textile effluents, in order to achieve extensive colour removal and high mineralisation rates.

The decomposition of ozone promoted by activated carbon is thought to be one of the steps of the activated carbon catalytic ozonation process. The first part of this work was dedicated to the study of the decomposition of dissolved ozone in the presence of activated carbons, focussing on the influence of their textural and chemical properties. Starting from the commercial activated carbon Norit GAC 1240 Plus (sample AC_0), two series of activated carbon samples, differing either in their surface chemistries or textural properties, were prepared, characterised and tested in the decomposition of dissolved ozone at different pH values (3, 5, 7, and 9). The rate of ozone decomposition was correlated with the textural and chemical properties of the activated carbon. In particular, among three activated carbon samples with different acid-base properties (AC_0, ACH_2 and $ACHNO_3$), the more basic one (ACH_2) was found to lead to higher decomposition rates.

The simultaneous use of ozone and activated carbon was found to be beneficial for the elimination of a series of organic aromatic compounds, such as aniline, sulfanilic acid and benzenesulfonic acid. Additionally, the mineralisation of oxalic and oxamic acids, which are final oxidation by-products of the previously mentioned compounds, was also significantly enhanced. In all cases, sample AC_0, which has basic characteristics comparatively to the oxidised sample $ACHNO_3$, led to the best results, mainly in terms of mineralisation. The ozonation of the carboxylic acids at acid pH was not significantly affected by the presence of $HO^{\bullet}$ radicals scavengers. Based on these observations, a reaction mechanism involving mainly surface reactions on the activated carbon was proposed.

Ceria (Ce-O), prepared by precipitation, and a ceria-activated carbon composite (AC_0-Ce-O) were also tested in the ozonation of the selected organic compounds. Both materials were found to be active ozonation catalysts. It was concluded that cerium oxide promotes the decomposition of ozone into $HO^{\bullet}$ radicals, which are the main oxidant species responsible for the oxidation of the compounds in the liquid phase. A significant synergic effect was observed between activated carbon and cerium oxide in the prepared composite. It was supposed that the existence of delocalized electrons on the basal planes of the activated carbon contributes to the formation of Ce (III) species, evidenced by XPS analysis, which are thought to be active for the decomposition of O_3 into $HO^{\bullet}$ radicals. In the ozonation catalysed by this composite, the reaction mechanism is believed to comprise both surface

reactions, similar to what occurs in activated carbon promoted ozonation, and also liquid bulk reactions involving $HO^{\cdot}$ radicals.

Catalytic ozonation notably enhanced the mineralisation of solutions of three commercial textile dyes: CI Acid Blue 113, CI Reactive Yellow 3 and CI Reactive Blue 5. However, no major improvements were observed in the rates of colour removal. Such results are explained by the high decolourisation potential of ozone. Comparatively to the performance of the commercial activated carbon, an enhanced mineralisation extent was achieved with the composite AC_0-Ce-O, which is explained by an improved ability to catalyse the decomposition of ozone into $HO^{\bullet}$ radicals.

The presence of high concentrations of inorganic ions with scavenging properties may restrain the results obtained in wastewater treatment by advanced oxidation processes. Activated carbon catalysts also promote surface oxidation reactions that do not involve the participation of $HO^{\bullet}$ radicals in solution, therefore being less affected by the presence of scavenger species. This was confirmed by testing the efficiency of the studied catalytic systems (activated carbon, ceria and ceria-activated carbon composite) in the mineralisation of real textile effluents.

Sumário

A ozonização catalítica é uma tecnologia emergente e poderosa para a eliminação de compostos orgânicos persistentes em águas e águas residuais. Do ponto de vista da aplicação prática, a integração da ozonização catalítica como tratamento terciário após os processos biológicos convencionais, quer aeróbios quer anaeróbios, é de grande interesse para se conseguir a despoluição completa dos efluentes líquidos, tais como os da indústria têxtil. O objectivo último desta tese foi fazer a avaliação da capacidade de depuração de efluentes têxteis utilizando alguns catalisadores de ozonização seleccionados, tendo em vista a necessidade de atingir níveis elevados de remoção de cor e de mineralização.

Pensa-se que a decomposição do ozono promovida pelo carvão activado é um dos passos do processo de ozonização catalisada por este material. A primeira parte do trabalho foi dedicada ao estudo da decomposição de ozono em fase aquosa na presença de carvão activado, dando especial atenção à influência das suas propriedades texturais e químicas. Partindo-se do carvão activado comercial Norit GAC 1240 Plus (amostra AC_0), prepararam-se e caracterizaram-se duas séries de amostras, uma constituída por carvões activados com diferentes químicas superficiais e a outra por materiais com propriedades texturais distintas. Todas as amostras foram testadas na decomposição de ozono dissolvido a vários valores de pH (3, 5, 7 e 9), tendo-se verificado que as velocidades de decomposição variavam significativamente com as propriedades mencionadas. Em particular, entre três amostras de carvão activado com propriedades ácido-base diferentes (AC_0, ACH_2 e $ACHNO_3$), a mais básica (ACH_2) foi a que originou maiores velocidades de decomposição.

Verificou-se que a utilização simultânea de ozono e de carvão activado era benéfica para a eliminação de vários compostos aromáticos, tais como a anilina, o ácido sulfanílico e o ácido benzenossulfónico. Além disso, mostrou-se que o grau de mineralização atingido em soluções dos ácidos oxálico e oxâmico, que são subprodutos finais de oxidação dos compostos anteriores, aumentava significativamente em relação à ozonização simples. Em todos estes casos, a amostra AC_0, que tem características básicas, ao contrário do carvão activado oxidado $ACHNO_3$, conduziu aos melhores resultados, principalmente em termos de mineralização. A ozonização catalítica dos ácidos carboxílicos a pH ácido não foi significativamente afectada pela presença de *scavengers* dos radicais $HO^{\cdot}$. Com base nesta observação, foi proposto um mecanismo reaccional que envolve sobretudo reacções à superfície do carvão activado.

O óxido de cério (Ce-O), preparado por precipitação, e um compósito óxido de cério-carvão activado (AC_0-Ce-O) foram também testados na ozonização dos compostos orgânicos seleccionados, já referidos. Ambos os materiais são catalisadores activos de ozonização. Concluiu-se que o óxido de cério promovia a decomposição do ozono em radicais $HO^{\bullet}$, que são as principais espécies responsáveis pela oxidação dos compostos na fase líquida. Foi observado um efeito sinérgico importante entre o carvão activado e o óxido de cério no compósito

preparado. Supõe-se que a existência de electrões deslocalizados nos planos basais do carvão activado contribui para a formação de espécies Ce (III) (facto demonstrado por análises de XPS), que se pensa serem activas para a decomposição do O_3 em radicais $HO^{\cdot}$. Na ozonização catalisada pelo compósito, acredita-se que o mecanismo envolve tanto reacções à superfície, semelhantes às que ocorrem na presença de carvão activado, como reacções no seio da fase líquida com a participação de radicais $HO^{\cdot}$.

A ozonização catalítica aumentou notavelmente o nível de mineralização conseguido em soluções de três corantes têxteis comerciais: CI Acid Blue 113, CI Reactive Yellow 3 e CI Reactive Blue 5. Contudo, não foram observadas grandes melhorias relativamente à ozonização simples no que respeita às velocidades de descoloração, o que foi explicado pela elevada aptidão do ozono para a remoção da cor. Em comparação com o desempenho do carvão activado comercial, foram atingidos níveis de mineralização superiores com o compósito AC_0-Ce-O, facto atribuído à grande capacidade deste material em catalisar a decomposição do ozono em radicais $HO^{\bullet}$.

A presença de concentrações elevadas de iões inorgânicos com características de *scavengers* pode limitar os resultados conseguidos por processos de oxidação avançada no tratamento de águas residuais. Entre outras, os catalisadores de carvão activado promovem reacções de oxidação na sua superfície, que não envolvem a participação de radicais $HO^{\bullet}$ em solução. Assim, são menos afectados pela presença de *scavengers*. Isto foi confirmado testando a eficiência na mineralização de efluentes têxteis reais dos catalisadores considerados neste trabalho (carvão activado, óxido de cério e compósito óxido de cério-carvão activado).

Résumé

L'ozonation catalytique est une technologie émergente et puissante au niveau de l'élimination des composés organiques persistants présents dans les eaux et eaux industrielles polluées. Du point de vue de l'application pratique, l'intégration de l'ozonation catalytique, comme traitement tertiaire postérieurement aux processus biologiques conventionnels, aussi bien aérobies qu'anaérobies, est de grand intérêt de façon à effectuer la dépollution complète des effluents liquides, comme ceux de l'industrie textile. L'objectif principal de cette thèse est l'évaluation de la capacité d´épuration des effluents textiles utilisant certains catalyseurs d'ozonation sélectionnés, ayant en vue la nécessité d'atteindre des niveaux élevés de suppression de couleur et de minéralisation.

Il semblait que la décomposition de l'ozone en présence de charbon actif est une des étapes du processus d'ozonation catalysé par ce matériel. La première partie de ce travail a été dédié à l'étude de la décomposition de l'ozone en phase aqueuse, avec une attention spéciale pour l'influence de ses propriétés texturales et chimiques. Partant d'un charbon actif commercial Norit GAC 1240 Plus (échantillon AC_0), deux séries d'échantillons ont été préparées et caractérisées, l'une constituée par des charbons actifs avec différentes propriétés chimiques superficielles, l'autre par des matériaux aux propriétés texturales distinctives. Tout les échantillons ont été testés au niveau de la décomposition de l'ozone dissous à différente valeur de pH (3, 5, 7 et 9), ayant ainsi été possible de vérifier que les vitesses de décomposition varient largement selon les propriétés mentionnées. En particulier, entre les trois échantillons de charbon actif aux différentes propriétés acide-base (AC_0, ACH_2 e $ACHNO_3$), la plus basique (ACH_2) a été celle qui a menée aux vitesses de décomposition les plus élevées.

Il a été vérifié que l'utilisation simultanée d'ozone e de charbon actif était bénéfique à l'élimination de composants aromatiques, comme l'aniline, l'acide sulfanilique e l'acide benzènesulfonique. Il a aussi été démontré que le degré de minéralisation atteint dans des solutions d'acide oxalique e oxamique, sous-produits finaux d'oxydation des produits antérieurs, augmentait de façon significative comparativement à l'ozonation simple. Dans tout les cas, l'échantillon AC_0, aux caractéristiques basiques, au contraire du charbon actif oxydé $ACHNO_3$, a conduit à de meilleurs résultats, principalement en terme de minéralisation. L'ozonation catalytique des acides carboxyliques à pH acide n'a pas été affectée de forme significative par la présence de *scavengers* des radicaux libres $HO^{\cdot}$. Ayant pour base ces observations, un mécanisme réactionnel a été proposé, qui implique surtout des réactions à la surface du charbon actif.

L'oxyde de cérium (Ce-O), préparé par précipitation, et un composite oxyde de cérium-charbon actif (AC_0-Ce-O) ont également été testés dans l'ozonation des composés organiques, déjà mentionnés. Les deux matériaux sont des catalyseurs actifs d'ozonation. Il a été conclu que l'oxyde de cérium favorise la décomposition de l'ozone en radicaux $HO^{\bullet}$, qui sont les principaux espèces actives responsables de l'oxydation des composés en phase liquide. Un effet synergique important entre le

charbon actif et l'oxyde de cérium a été observé au niveau du composite préparé. Probablement, l'existence d'électrons délocalisés des plans de base du charbon actif contribuent à la formation d'espèces Ce (III) (prouvé par des analyses de XPS), que sont actives dans la décomposition de O_3 en radicaux $HO^{\cdot}$. Au niveau de l'ozonation catalysée par le composite, il est probable que le mécanisme implique autant des réactions à la surface, de façon identique à celles obtenue en présence de charbon actif, ainsi comme des réactions au sein de la phase liquide avec la participation de radicaux $HO^{\cdot}$.

L'ozonation catalytique a remarquablement augmenté le niveau de minéralisation atteint dans des solutions de trois colorants textiles commerciaux: CI Acid Blue 113, CI Reactive Yellow 3 e CI Reactive Blue 5. Cependant, aucune grande amélioration n'a été observée relativement à l'ozonation simple plus précisément quant aux vitesses de décoloration, ce qui a été expliqué par la grande capacité de l'ozone dans l'élimination de la couleur. En comparaison avec le comportement du charbon actif commercial, des niveaux de minéralisation plus élevés ont été atteints avec le composite AC_0-Ce-O, fait attribué à la grande capacité de ce matériel dans la décomposition de l'ozone en radicaux $HO^{\cdot}$.

La présence de concentrations élevées de certains ions inorganiques aux caractéristiques de *scavengers* peut limiter les résultats atteints par les processus d'oxydation avancée dans le traitement des eaux résiduelles. Entre autres, les catalyseurs de charbon actif promeuvent les réactions d'oxydation à la surface, qui n'impliquent pas la participation de radicaux $HO^{\cdot}$ en solution. Ainsi, ils sont moins affectés par la présence de *scavengers*. Ceci a été confirmé par l'étude de l'efficacité de la minéralisation d'effluents textiles réels en présence des catalyseurs considérés dans ce travail (charbon actif, oxyde de cérium et composite oxyde de cérium-charbon actif).

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Part I
Introduction

The first part of this thesis provides a brief overview of the textile industry in Portugal, focusing on the identification of the major environmental issues associated to this industrial sector. Special emphasis is given to the water related problems, which include water consumption and consequent wastewater generation. The general characteristics of the textile liquid effluents are listed along with a description of the most problematic chemical products present in textile wastewater. A short description of the available technologies for the treatment of those liquid effluents is also presented. The chemistry of ozone in water and the decomposition of ozone in the aqueous phase are reviewed, focusing on the role of activated carbon in the catalytic decomposition of dissolved ozone. An overview of the catalytic ozonation processes applied to the mineralisation of organic compounds is presented, highlighting the role of the activated carbon as ozonation catalyst. The catalytic activity of several metal oxides and supported metal oxides is also reviewed. Finally, the main objectives of this work and the thesis outline are presented.

1 Introduction

1.1 General overview of the textile industry and associated environmental problems

The textile industry is composed of a wide number of sub-sectors covering the entire production cycle from the fabrication of raw materials (man-made fibres), to semi-processed materials (yarns, woven and knitted fabrics with their finishing process) and final products (home textiles, carpets, clothing and textiles for industrial use) [1]. The main production stages: yarn formation, fabric formation, wet processing, and fabrication, are highlighted in the process flow chart shown in Figure 1.1.

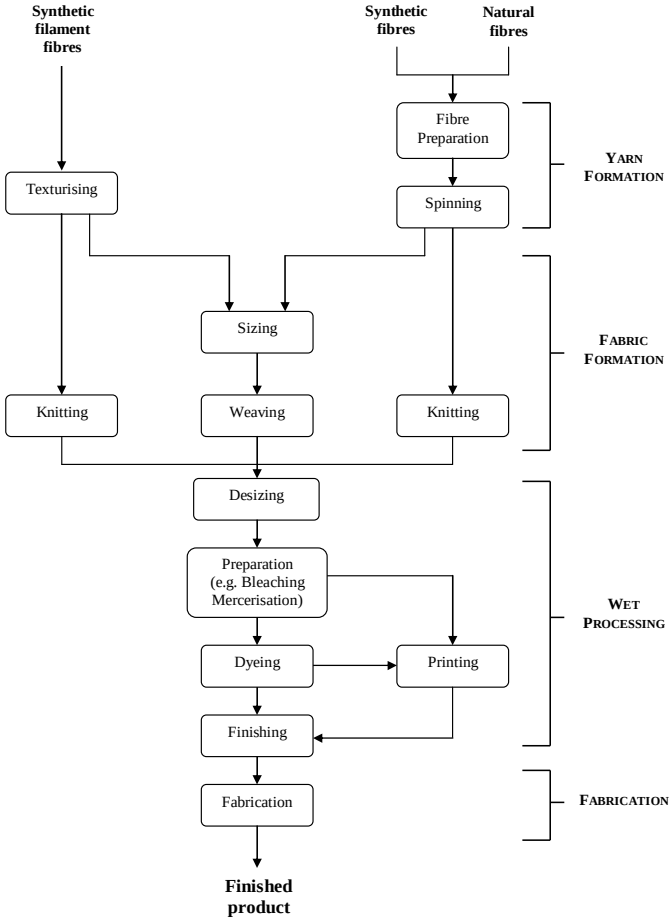

Figure 1.1 Typical textile processing flowchart (adapted from [2]).

The textile and clothing processing industry is one of the most important industrial sectors in the Portuguese economy. The implementation of the first factories dates back to the XVIII century, and textile industry has long been one of the main industries in terms of employment and internationalisation. During the sixties, Portugal became one of the major worldwide exporters of textiles and clothing. However, the most important development occurred during the 1980s and the 1990s, with the technological upgrade of the sector supported by governmental and European financial funding [3].

According to the national association of textiles and clothing (ATP - Associação Têxtil e Vestuário de Portugal) [4], in the year 2006, the textile and clothing processing industry represented 25% of the employment in the transformation industry, and was responsible for 12% of the total national exportations. It also represented 10% of the total production of the transforming industry. Portugal has more than three thousand companies working in all the subsectors of the textile and clothing industry. Some of them are vertical factories, covering the entire manufacturing process from yarning to final product. However, the major percentage consists of small and medium companies dedicated to parts of the manufacturing process, such as dyeing and finishing. Concerning the geographical location (Figure 1.2), there is an obvious concentration of textile plants in the northwest region of the country, where ca. 70% of the factories are located. In the region of Covilhã there is another cluster of textile plants, mostly dedicated to the processing of wool [3, 4].

The textile manufacturing is a water intensive industry due to the large amounts of water used. According to data gathered by the technological centre of the textile and clothing industries of Portugal (CITEVE - Centro Tecnológico das Indústrias Têxtil e do Vestuário de Portugal), the water consumption in the Portuguese textile industries varies between 90000 m^3/year and 800000 m^3/year, which corresponds to a specific water consumption of 50 to 250 m^3/ton of textile product [5]. This justifies the implementation of such factories in the valleys of rivers Ave and Cávado, and in the region of Fundão.

Figure 1.2 Geographical distribution of the textile and clothing industry in Portugal [3].

Additionally, textile industry is also chemical intensive, due to the vast range of chemical products applied in the manufacturing process, which, associated to the water consumption, makes it one of the largest industrial producers of wastewater requiring adequate treatment [6]. The great concentration of textile plants in the valley of river Ave (ca. 1/3 of the industrial units of the region), and its inherent environmental problems associated to the generalised lack of treatment for the generated liquid effluents, led to the implementation of SIDVA – Sistema Integrado de Despoluição do Vale do Ave. This consists of an integrated system for the collection and treatment of mixed industrial and domestic wastewater, with the aim of promoting the depuration of river Ave [5]. Presently, the three wastewater plants (WWTP) belonging to SIVDA (Figure 1.3) have basically the same treatment process, which consists of the following steps: screening for the removal of suspended solids, homogenisation and equalisation, neutralisation, biological treatment with activated sludge, physical-chemical process and filtration on sand filters. Additionally there is a separate line for the treatment of the biological sludge originated in the water treatment [7].

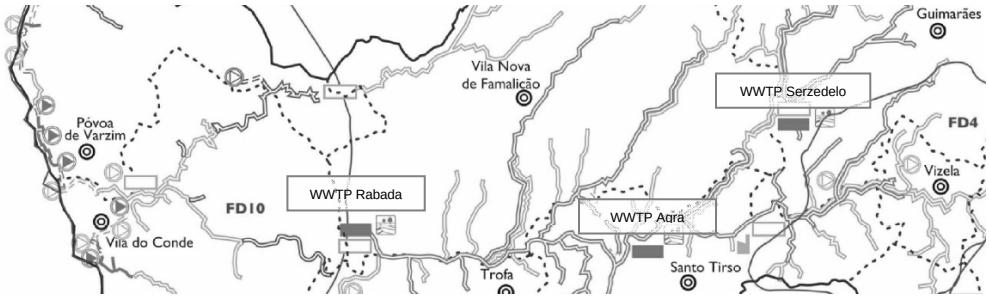

Figure 1.3 Geographical location of the wastewater treatment plants from SIDVA (adapted from [8]).

In a global scale, the main environmental issues arising from the activities in the textile industry concern, primarily, emissions to water and air, and energy consumption. Regarding emissions to air, the release of volatile organic compounds resultant from the use of organic solvents, and the emission of CO_2, SO_x, NO_x and particulates, associated with the on-site burning of fossil fuels to produce thermal energy, are the main environmental issues. Energy is consumed primarily in raising the temperature of the baths (e.g. pre-treatment operations, dyeing, etc.) and in drying. To this aim, steam is produced on-site. Among these environmental issues, water related problems are those raising deeper concern [1]. The textile industry uses water as the principal medium for removing impurities, applying dyes and finishing agents, and for the generation of steam. The main worry is, therefore, about the amount of water discharged and its chemical load [1].

In the textile processing industry, the main sources of water consumption, and consequent wastewater generation, are the washing and bleaching of natural fibres, the dyeing and subsequent rinsing operations, and finishing steps [9]. In general, the water consumption can vary between 25 and 200 L per kg of textile substrate, depending on the operation, machinery and textile substrate being processed. As an example, the specific consumption of water in the bleaching, dyeing, rinsing, washing and softening of cotton knit, in discontinuous processes, lies between 100 and 150 L per kg of textile substrate [10]. Concerning the pollution degree, a large percentage of the total emission load is attributable to substances that are already in the raw material before it enters the finishing process sequence. Typically these are sizing agents, preparation agents, and natural fibres impurities. The additional input

of chemicals and auxiliaries used at the finishing mills can be up to 1 kg per kg of processed textiles. Among the vast range of products applied during the process, the highest loads arise from salts, detergents and organic acids. Dyestuffs do not represent a significant load compared to other substances used in the process. Nevertheless, dyes are responsible for the colour of the effluent, which is both an aesthetic and ecological problem [1], and are usually resistant to the conventional wastewater treatment processes.

1.2 The nature of textile effluents

The quantity of spent water and chemical load applied is dependent on the process step; therefore, the liquid effluents originated in the textile and clothing industry are mainly characterised by huge variations both in flow and chemical composition [11]. Generally, the composition of raw mixed wastewater is characterised by high temperature and conductivity, alkaline pH, intense colouration, due to unfixed dyes, and high organic load, including persistent and toxic substances [12]. Given the variety of fibres and chemical products used in the textile processing industry, the resultant liquid effluents are of great chemical complexity and diversity [9].

The products used in the textile wet processes are mainly dyes and auxiliary chemical products, which include the vast array of substances that contact with the fibre during the process and those that confer specific properties to the fabrics. Among them, some react with the fibre, others are totally or partially retained by the fibre, but most of them act simply as mediators and, therefore, are present in the exhausted baths [10]. The most relevant categories of products are listed in Table 1.1, together with a brief description of their function.

Table 1.1 Most significant chemical products used in the textile processing and corresponding main function (adapted from [10]).

Chemical product	Function
Sizing agents	Improve the mechanical resistance of the fibres during the yarning process
Bleaching agents	Remove natural colour of the fibres
Surfactants	Decrease surface tension of the fibres improving contact with water
Softeners	Softening the fibres
Sequestrants	Form complexes with metallic ions to prevent their interference in the process
Salts (NaCl, Na_2SO_4)	Neutralization of charges (electrolyte)
NaOH	Purification and mercerization of cotton; pH adjustment in dyebaths
Acids and alkalis	pH adjustment
Dyes and pigments	Colouration (dyeing and printing)

The desizing operation, which consists in the removal of sizing products from the fibre, is one of the processing steps that originate highly polluted wastewater. Sizing products are used to confer fibres a high mechanical resistance, but are not retained in the fibre. During the desizing step, these products are washed away, significantly increasing the organic load of the effluent [5]. In the cotton processing industry, the following characteristics of the effluents resultant from desizing step have been reported [11]: BOD_5 (5-day Biological Oxygen Demand) = 1595 mg O_2/L, COD (Chemical Oxygen Demand) = 3320 mg O_2/L, TDS (Total Dissolved Solids) = 5650 mg/L. The use of starch and starch based sizing products is environmentally friendly, as they are easily biodegradable. Synthetic sizing agents such as polyvinylalcohol (PVA) are not biodegradable, but they can be recovered by ultrafiltration [5].

Most textile wet processes, such as sizing, desizing, dyeing and washing, consume high amounts of surfactants (detergents, dispersing agents, emulsifiers, wetting agents). These products are not retained in the fibres, and, therefore the total amount used is present in the exhausted baths. They impart high organic load to the effluent and lead to the formation of foams [10]. A large fraction of the surfactants

used are alkyl phenol ethoxylates, which are biodegraded to alkylphenols. However, alkylphenolic compounds are persistent, bio-accumulative and much more toxic than the initial surfactant. Strict limit discharges are applied for surfactants, especially for alkylphenol ethoxylates (in Portugal: 0.5 mg/dm^3 of phenol equivalents) [9].

In practice many fibres, including cotton, require bleaching, either to remove dirt, or to remove the natural colour of the fibres. The bleaching operation is carried out with oxidants, such as sodium hypochlorite or hydrogen peroxide, and is one of the processing steps with higher water consumption [11]. Chlorinated bleaching agents are associated with the formation of adsorbable organic halogens (AOX). Given their carcinogenic nature, the discharge of AOX is restricted in a number of countries [9].

The high pH of the raw textile wastewater is due to the use of large amounts of sodium hydroxide. This is used in concentrated form in the cotton purification and mercerization, and to adjust the pH in cotton dyeing with reactive dyes [5]. Other inorganic compounds such as sulphuric acid, chloridric acid, and sodium carbonate, as well as organic acids (acetic and formic) are used to adjust pH and remove finishing products, and are not fixed in the fibres. High loads of organic acids are generally present in textile effluents. Large amounts of salts, such as sodium chloride (NaCl) and sodium sulphate (Na_2SO_4), are used as dyeing auxiliaries and are not fixed in the fibre. They are responsible for the high conductivity found in the textile effluents [5]. One possible way to eliminate them is through membrane separation techniques.

Finishing steps include several physical or chemical processes performed on fibre, yarn, or fabric, to improve its appearance, texture or performance. A large number of finishing auxiliaries are used, e.g. for fire-, moth- or water-proofing, as well as softening agents [9]. Such products are fixed in the fibre, but a certain amount is present in the exhausted baths.

Effluents from most textile dyeing mills generally have a dark reddish-brown colour [6] due to colour residues, which is one of the most problematic issues concerning wastewater from this industrial sector. Even though dyes do not impart a significant organic load to the textile effluents, their presence in natural water courses causes negative aesthetic impact. Therefore, colour in liquid effluents from textile dyeing and printing operations is being increasingly regulated. Modern textile dyes are

required to have a high degree of chemical and photolytic stability so that they maintain their structure and colour. One consequence of this stability is that they are not readily degraded under the aerobic conditions prevailing in the biological treatment plants, as is the case of activated sludge systems [13]. Therefore a tertiary treatment is required for proper colour elimination.

The classification of dyes is based either on the chemical nature of the molecule chromophore, being azo and anthraquinone the most common ones, and on the mode of application in the dyeing process. According to the latter, dyes are classified as acid, reactive, basic or cationic, disperse, direct, metal-complex, vat or sulphur dyes. Among them, reactive dyes are one of the most representative classes, as they are used in the dyeing of cotton. Of all textile substrates, cotton is the mostly used, and 50% of it is dyed with reactive dyes. From an ecological point of view, this class of dyes is also the most unfavourable, as the effluents produced are frequently heavily coloured and contain high concentrations of salts [14]. Reactive dyes have a low fixation degree compared to other types of dyestuff, since the functional group also bonds to water, becoming hydrolyzed [14, 15]. Up to 50% of the dye concentration may remain in the exhausted dyebath [13] (see Table 1.2).

Table 1.2 Estimated degree of fixation for different dye/fibre combinations [13].

Dye class	Fibre	Degree of fixation (%)	Loss to effluent (%)
Acid	Polyamide	80-95	5-20
Basic	Acrylic	95-100	0-5
Direct	Cellulose	70-95	5-30
Disperse	Polyester	90-100	0-10
Metal-complex	Wool	90-98	2-10
Reactive	Cellulose	50-90	10-50
Sulphur	Cellulose	60-90	10-40
Vat	Cellulose	80-95	5-20

Concerning the chemical structure, azo dyes, largely used in the textile industry, have serious environmental impact due to the carcinogenic nature of their precursors and degradation products. According to the literature [9], among more than 100 azo dyes tested, only a few were biodegraded aerobically. Under anaerobic

conditions, however, azo dyes are converted into aromatic amines through the reduction of the $-N=N-$ bond. The resultant by-products are not further metabolised under anaerobic conditions but, may be oxidised in aerobic environment, under specific conditions. Even so, the biodegradation of such aromatic amines in aerobic reactors has proven to be difficult. Therefore, additional treatment stages are necessary to ensure mineralisation of azo dyes [16]. Different classes of dyes may also be partially degraded under anaerobic conditions, though less readily than azo dyes. The complexity of the dye structure and the number of sulfonate groups may decrease the rate of biodegradation [9].

Given the great chemical diversity and complexity of the liquid effluents generated from textile processing and dyeing operations, appropriate treatment is required before the discharge in natural water courses. The next section presents a short overview on the available and emerging wastewater treatment technologies. Emphasis is given to oxidation treatments as part of integrated wastewater treatment processes.

1.3 Conventional and emerging technologies for the treatment of textile wastewater

Among the vast array of existent wastewater treatment techniques, none has emerged as a simple, cost-effective and universally applicable method to the treatment of textile effluents. The selection of the wastewater treatment process, or the configuration of a wastewater treatment plant must consider the initial characteristics of the effluent, the desired final quality, which is dependent on the fate of the treated stream (discharge or reutilisation), as well as sludge production and subsequent handling costs, installation, operation and maintenance costs, and long-term system reliability [5].

Currently, most of the wastewater generated in the Portuguese textile industry is mixed and discharged to municipal wastewater treatment plants after pre-treatment, in order to meet discharge consents. However, some textile companies run their own wastewater treatment plants. Typically, the treatment process in an industrial wastewater plant is a three step treatment comprising primary, secondary and tertiary or polishing treatments. For the textile industry effluents, the primary treatment consists in the removal of small dimension suspended solids,

homogenisation and pH neutralisation. As an example, the pH of effluents from processing and dyeing of cotton fibres are typically highly alkaline. The neutralisation is accomplished with sulphuric acid and CO_2, which is used to achieve a more precise pH adjustment [5].

The secondary step is the main treatment and is usually accomplished with biological processes, which reproduce the phenomena of self-purification existent in nature [14]. Biological treatments are classified as aerobic and anaerobic, depending on whether they use oxygen or not. Among the existent aerobic biological processes, activated sludge is the most widely used [5].

Conventional aerobic biological processes used in the textile industry can lead to high COD reduction, but are not effective for total mineralisation, as a result of the low biodegradability of most dyes and chemicals present [14]. In fact, aerobic biological treatments are usually unsuccessful for significant dyestuff removal, beyond the adsorbing capacity of the biomass, mainly due to the fact that dyes are designed to be bio-resistant [17]. Frequently, a polyelectrolyte is added during the activated sludge process in order to enhance the colour removal. In spite of the good results achieved in terms of decolourisation, the continuous addition of reagents and the production of large volumes of sludge, substantially increase the treatment costs.

According to the literature, certain dyes are susceptible to anaerobic decolourisation [17]. Therefore, an anaerobic step followed by an aerobic step may represent a significant advance in biological treatments towards enhanced decolourisation efficiency [17]. Anaerobic biological processes present several advantages comparatively to aerobic systems. The production of sludge, even for high organic load, is significantly lower comparatively to aerobic systems. An anaerobic stage before the aerobic treatment my protect the aerobic bioreactor from toxic compounds, reduce the formation of foams, and other problems that destabilize aerobic systems, and reduce the costs related to sludge disposal [5]. Nonetheless, despite the numerous laboratory scale trials showing the potential of anaerobic treatment for colour removal, large-scale installations equipped with an anaerobic pre-treatment do not generally achieve full decolourisation [9].

The above mentioned treatment steps are usually not sufficient to meet established discharge consents. Moreover, if water reuse is to be considered, total decolourisation, extensive removal of persistent pollutants and dissolved salts must

be reached. Consequently, a tertiary step must be added to the treatment process. To meet this requirement there is a variety of treatment techniques ranging from adsorption and membrane separation to oxidation processes. Table 1.3 lists the most common post-treatment processes together with the main advantages and limitations.

Table 1.3 Evaluation of various techniques for the tertiary treatment of textile effluents.

Process	Performance	Limitations
Membrane separation	High performance; reuse of water and salts	Handling and disposal of concentrate stream; costs
Adsorption (carbon, clay, biomass)	Depending on the sorbents can be effective and cheap	Pollution transfer; high disposal or regeneration costs
Coagulation-Flocculation	Full decolourisation; elimination of insoluble dyes	Not always effective; sludge disposal
Electrolysis	Full decolourisation; cheap process	Foaming and electrode lifespan; currently in lab-scale
Ozonation	Full decolourisation; water reuse; no sludge production	High installation costs
Fenton oxidation	Full decolourisation	Sludge production; running costs
Photocatalysis	Partial colour removal; detoxication	High costs; only as final polishing step

Microfiltration, ultrafiltration, nanofiltration and reverse osmosis are the available membrane separation techniques. Cost and complexity are the main factors limiting the application of membrane technology. In general, it can be said that membrane systems are costly, operation and maintenance intensive, and generate a concentrated stream requiring further treatment. On the other hand, they offer the appeal of recovering and reusing chemicals and dyes and producing reusable water [17]. The successful use of full-scale ultrafiltration to recover and reuse polyvinyl alcohol, indigo dye and to purify NaOH has been reported [5]. Membrane separation method is also one of the few alternatives for the removal of dissolved salts.

Coagulation/flocculation processes, consist in the addition of chemical reagents that lead to the aggregation of colloidal particles that are further removed by sedimentation, flotation or filtration. These are commonly used as tertiary treatment to eliminate organic substances and remove colour from textile effluents, enabling the successful elimination of insoluble dyes. Despite their effectiveness, such physical-chemical processes generated high amounts of sludge that require appropriate treatment and disposal [14].

Adsorption techniques are only feasible when used as a final polishing treatment as part of an integrated wastewater treatment process. The wide variety of adsorbents studied includes activated carbon, inorganic materials such as silica or clay, ion-exchange resins, and biosorbents such as chitin. Among them, activated carbon is the most universal and widely applied. Its high surface area and unique surface chemical properties make it suitable for the removal of several organic compounds form liquid effluents. Depending on the effluent characteristics, activated carbon can become quickly saturated, requiring regeneration or substitution [14, 17]. Further appropriate disposal is necessary in the latter situation.

From an environmental point of view, oxidative, rather than separation methods should preferably be used for textile wastewater treatment. Suitable colour removal and elimination of recalcitrant pollutants can be accomplished by powerful oxidising methods such as chlorine, ozone, Fenton's reagent (H_2O_2 and ferrous sulfate) or UV assisted techniques. Although effective and low cost, chlorine methods have the potential of forming undesirable organochlorine compounds. UV radiation has been tested in combination with H_2O_2 or solid catalysts, such as TiO_2, for the decolourisation of dye solutions. The limited penetration of UV radiation into strongly coloured effluents prevents the use of UV assisted techniques. To overcome this limitation, the use of UV technology as a post–treatment after ozonation, or the combination of O_3 and UV techniques have been suggested [9]. The cost of the Fenton's reagent approach and the large amount of metal containing sludge formed makes this process far less attractive. Among the available destructive treatments, ozonation and ozone-initiated destruction techniques are becoming increasingly important as a final treatment technology to improve colour removal and the elimination of other persistent pollutants present in bio-treated effluents [18]. Ozone molecule is selective and attacks, preferentially, aromatic structures and unsaturated bonds, such as those of the dye chromophores, leading to fast decolourisation. The typical oxidation products are carboxylic acids and

aldehydes, which explains the low COD removal and possible BOD increase during the ozonation [5]. There has been much research into colour removal from textile effluents, both using complex real effluents, simulated effluents and simple dye solutions [15]. Although installation costs are relatively high, ozone has proven to be, by far, the most effective and fast chemical oxidation method to meet the strict colour discharge limits of many industrialised countries [9].

In conclusion, there are many methods available for the effective depuration and total decolourisation of textile wastewater and some are still under intense research. According to the previous descriptions, a promising treatment process would include a biological anaerobic/aerobic combination followed by an oxidation polishing step [17].

1.3.1 Ozonation applied to the treatment of textile wastewater

In the beginning of the 1980s, Rice and Browning [19] published a comprehensive compilation of cases about the application of ozone in the treatment of wastewater originated in a wide range of industries, such as pharmaceutical, textile, pulp and paper, chemicals manufacturing, petroleum refineries, etc. In the past few years a vast number of papers dealing with the application of ozonation to the treatment of several wastewater streams has been published [20].

Due to its extremely high oxidation potential and selectivity to attack chromophores and unsaturated bonds, ozone is highly efficient in degrading dye molecules. Thus, oxidation using ozone has been one of the most commonly evaluated methods for dye colour removal over the past 30 years [17]. The lack of sludge production, the potential to accomplish both decolourisation and COD reduction in a single step, and ease of operation, are some of the reasons that validate ozonation as a promising technique for the enhanced treatment of textile wastewater.

Considering the effluents produced in the textile industry, the presence of several dyebath additives such as surfactants, inorganic salts, and sequestering agents, may inhibit removal efficiencies and dramatically increase the ozone consumption rates. As a consequence, the process may become extremely expensive [9]. Because of the large amount of ozone potentially needed, ozonation is not usually a cost-effective technology if used as the main treatment operation for wastewater. Consequently, ozonation processes should be used as a complementary or final

oxidation treatment [9]. Among the available oxidative destructive processes, ozonation is becoming increasingly important as a final (post)treatment technology to improve colour removal and the elimination of other persistent pollutants presented in bio-treated effluents [18].

In a literature review of technologies for the treatment and reuse of wastewater from the textile wet-processing industry, Vandevivere et al. [9] presented several examples of the use of ozonation as an integrated step in the treatment of effluents from textile plants. In the reported examples, ozone was generally used as a tertiary treatment, especially to accomplish effective decolourisation. In an Italian wastewater treatment plant (Alto Lura WWTP, Como), a mixture of 75% textile and 25% municipal wastewater is treated with a sequence of pre-denitrification, activated sludge, sand filtration and ozonation. The latter step was built in order to reduce surfactants and colour in the final effluent. These goals are achieved with an ozone dose of 20 mg/dm^3, but unwanted by-products, such as aldehydes, are formed and their removal requires an additional treatment step. In fact, ozone is capable of oxidising a vast range of organic compounds, but typically single ozonation rarely leads to total mineralisation. Instead, saturated compounds such as aldehydes and small chain carboxylic acids are formed from the partial oxidation of the initial organic compounds present in solution.

One of the advantages of the use of ozonation as polishing treatment is the possibility of reusing the water in the textile processes. Successful cases of water reuse, both at the pilot-scale and industrial scale, are reported in the literature [9].

Numerous laboratory-scale experiments have documented the feasibility of ozonating spent dyebaths separately, and reusing the decolourised effluent several times with excellent colour reproducibility. In the case of spent reactive dyebaths, in addition to the reuse of water, the possibility of reusing salts, would allow even higher cost savings. However, in such cases, due to the high concentration of dyes (several hundreds ppm) and the presence of dyeing auxiliaries, the amount of ozone required for nearly complete colour removal is quite high, and may become prohibitively expensive. For that reason, reports on full-scale application of a reuse strategy involving separate ozonation of dyebath effluents are lacking [9].

The nature of the compounds present in water determines the degree of reactivity with ozone. Compounds with specific functional groups such as aromatic compounds or unsaturated hydrocarbons are prone to ozone attack, while other

compounds such as saturated hydrocarbons, alcohols, aldehydes or carboxylic acids can be considered resistant to ozone attack. In the latter case, ozone indirect reactions, which involve the formation of $HO^{\bullet}$ radicals, may play an important role. Ozone based advanced oxidation processes, which combine ozone with UV radiation or hydrogen peroxide, as well as catalytic ozonation, are emergent technologies that significantly improve the conventional method of ozone treatment [17].

1.4 Ozone chemistry and reactivity in water

The high reactivity of ozone can be attributed to the electronic configuration of the molecule. The two extreme forms of resonance structures of ozone molecule are illustrated in Figure 1.4. The absence of electrons in one of the terminal oxygen atoms in some of the resonance structures confirms the electrophilic character of ozone. Conversely, the excess negative charge present in some other oxygen atom imparts a nucleophilic character to the molecule [20, 21].

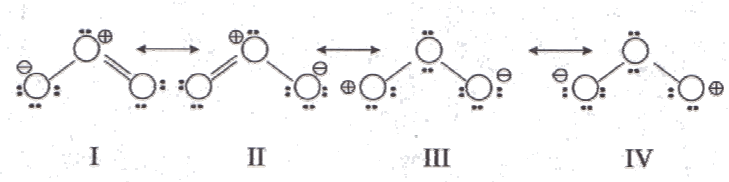

Figure 1.4 Resonance structures of the ozone molecule [20].

The reactions undergone by ozone in water are divided in three main categories: oxidation-reduction reactions, dipolar cycloaddition and electrophilic substitution reactions. The possibility of occurring nucleophilic addition reactions has only been confirmed in nonaqueous systems [20].

Ozone has one of the highest standard redox potential, only lower than those of fluorine, atomic oxygen or hydroxyl radical (Table 1.4). Because of its high standard redox potential, the ozone molecule has a high capacity to react with numerous compounds by means of redox reactions. Some of these reactions occur by explicit electron transfer, while most of them occur by an oxygen transfer from the ozone molecule to the other reactant.

Table 1.4 Standard redox potential of some oxidant species (adapted from [20]).

Oxidant species	E^0 (Volts)	Relative potential to ozone
Fluorine	3.06	1.58
Hydroxyl radical	2.80	1.45
Atomic oxygen	2.42	1.17
Ozone	**2.07**	**1.00**
Hydrogen peroxide	1.77	0.85
Permanganate	1.67	0.81
Chlorine	1.36	0.66
Bromine	1.09	0.53
Oxygen	0.40	0.19

Addition reactions occur between a compound with available π electrons (such as unsaturated compounds) and a molecule with electrophilic character, such as ozone. Reactions between ozone and olefinic compounds follow the Criegge mechanism that consists in the attack of one ozone molecule on the C-C double bond. Ozone can also react with aromatic compounds through a similar mechanism, leading to the breakup of the aromatic ring. However, this reaction is dependent on the stability of the ring and, therefore, less probable to occur than the electrophilic attack.

In electrophilic substitution reactions, ozone attacks one nucleophilic position of the organic molecule, such as an aromatic compound, resulting in the substitution of one part of it. Thus, after electrophilic substitution, the molecule retains its aromatic properties. The reactivity of aromatic compounds towards ozone is strongly affected by the nature of the substituting groups, which can activate or deactivate the ring. Activating groups such as –OH or $–NH_2$ promote the substitution of hydrogen atoms in *-ortho* and *-para* positions of the ring, while deactivating groups such as $–NO_2$, $-HSO_3$ or halogens, facilitate the substitution in the *-meta* position. Theoretically, *-ortho* and *-para* positions have the highest probability of undergoing electrophilic substitution reaction. Thus, the ozonation of aromatic compounds with activating functional groups is faster than that of compounds with deactivating

groups. An example is the direct ozonation of phenol and benzene, which rate constants (20 ºC, pH 7) were found to be 2 x 10^6 and 3 $M^{-1}s^{-1}$, respectively [20].

In some cases, free radicals are formed from the ozonation reactions. These free radicals propagate themselves by chain mechanisms to yield hydroxyl radicals ($HO^{\bullet}$), which participate in the oxidation reactions. Ozone reactions in water are, thus, classified as direct and indirect reactions. Direct reactions occur between ozone molecules and other chemical species (M), while indirect reactions are those between the $HO^{\bullet}$ radicals (formed from the decomposition of ozone or from other direct ozone reactions) and compounds present in water. In contrast to other conventional oxidant species, the hydroxyl radical is capable to completely oxidise (i.e. mineralise) even the less reactive pollutants. It reacts non-selectively with organic compounds, mainly by means of electrophilic addition to unsaturated bonds, addition to aromatic rings, abstraction of hydrogen or by electron transfer. The rate constants of most reactions between $HO^{\bullet}$ and organic species are usually in the order of 10^6-10^9 M^{-1} s^{-1} [22]. Mineralisation end products are generally carbon dioxide, water and inorganic ions.

Since the first model proposed by Weiss in 1935 [23], numerous studies have been developed to clarify the mechanism of decomposition of ozone in water. Presently, the mechanism proposed by Staehelin and Hoigné [24] is generally accepted for the decomposition of dissolved ozone, but alternative reaction steps have been proposed by other authors. A review of the proposed mechanisms is presented in [20].

The reactions of ozone with hydroxide (1.1) and hydroperoxide ions (1.2) are generally accepted as the main initiation steps of the ozone decomposition chain mechanism. Reactions between ozone and UV radiation, hydrogen peroxide, reduced metal ions, or heterogeneous catalysts can also initiate the decomposition of ozone in aqueous solution.

Initiation:

$$O_3 + HO^- \rightarrow HO_2^- + O_2 \qquad (1.1)$$

$$O_3 + HO_2^- \rightarrow HO_2^{\bullet} + O_3^{-\bullet} \qquad (1.2)$$

The reaction between ozone and the superoxide radical ($O_2^{-\bullet}$) is one of the main steps of the propagation of ozone decomposition, leading to the formation of the hydroxyl radical.

Propagation:

$$HO_2^{\bullet} \leftrightarrow O_2^{-\bullet} + H^+ \quad (1.3)$$

$$O_3 + O_2^{-\bullet} \rightarrow O_3^{-\bullet} + O_2 \quad (1.4)$$

$$O_3^{-\bullet} + H^+ \leftrightarrow HO_3^{\bullet} \quad (1.5)$$

$$HO_3^{\bullet} \rightarrow HO^{\bullet} + O_2 \quad (1.6)$$

$$O_3 + HO^{\bullet} \rightarrow HO_2^{\bullet} + O_2 \quad (1.7)$$

The chain reaction is maintained by the promoters, which are all organic and inorganic molecules capable of transforming $HO^{\bullet}$ radicals into superoxide radicals. Common promoters include methanol, carbohydrates, formaldehyde, formate ions, humic acids, etc [25].

The ozone decomposition chain can be terminated when hydroxyl radicals react with inhibitors, which are compounds capable of consuming $HO^{\bullet}$ radicals without regenerating the superoxide radical. The more common inhibitors include tertiary alcohols (e.g. *tert*-butanol), or carbonate and bicarbonate ions. These are also called hydroxyl radical scavengers, because their presence limits or inhibits the action of these radicals on the target compounds. *Tert*-butanol is a well known radical scavenger, as it reacts with $HO^{\bullet}$ at a rate constant of 5×10^8 M^{-1} s^{-1} [26], which is in the range of the rate constants of reactions between $HO^{\bullet}$ and organic compounds.

Bicarbonate (HCO_3^-) and carbonate ions (CO_3^{2-}) react with hydroxyl radicals to produce carbonate radical ions via the following reactions [22]:

$$HCO_3^- + HO^{\bullet} \rightarrow CO_3^{-\bullet} + H_2O \qquad k = 8.5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1} \quad (1.8)$$

$$CO_3^{2-} + HO^{\bullet} \rightarrow CO_3^{-\bullet} + HO^- \qquad k = 3.9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1} \quad (1.9)$$

As demonstrated by the values of the reaction rate constants, carbonate ions are stronger scavengers than bicarbonate ions. Therefore, the bicarbonate concentration present in an ozone wastewater treatment process is less important than the concentration of carbonate. This highlights the importance of pH in ozonation. Even

though the rate constants of these scavenging reactions may not be very high when compared to other $HO^{\bullet}$ reactions with organic pollutants, their inhibiting effect can be high depending on their concentration in solution. The presence of carbonates in natural waters reduces the efficiency of ozonation to oxidise refractory contaminants.

To sum up, in an ozonation process two possible pathways have to be considered: the direct pathway through the reactions with molecular ozone, and the radical pathway through the reactions with hydroxyl radicals generated in the ozone decomposition (see Figure 1.5).

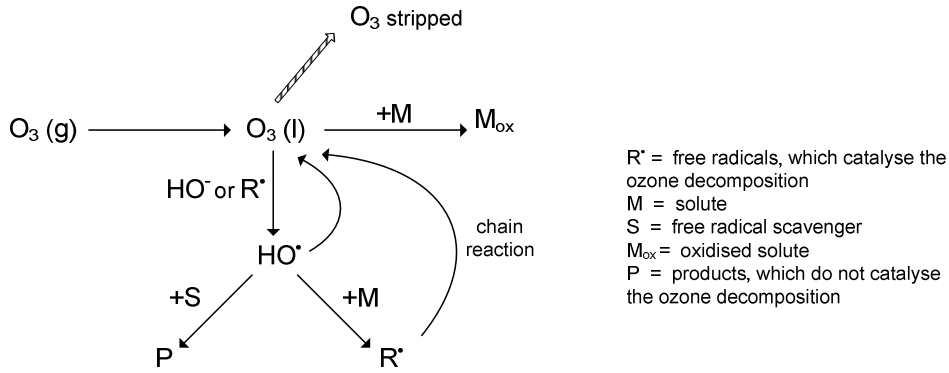

Figure 1.5 Reactions undergone by ozone in the aqueous phase (adapted from [27]).

The importance of each mechanism is dependent on several factors such as temperature, pH and chemical composition of the aqueous solution. The ozone decomposition rate depends strongly on the pH of the solution and on the nature of the substances present in water. Normally, under acidic conditions (pH < 4) the direct pathway rules, whereas for pH > 10 mainly the radical pathway is present. Under neutral conditions, both pathways can be important [28]. In some cases, even at acid conditions, the radical oxidation can be significant, depending on the contaminants present. Both pathways should always be considered when developing a treatment scheme. Due to the importance of the generation of $HO^{\bullet}$ radicals to the oxidation of organic compounds, the decomposition of ozone in water has been subject of intense research. This issue will be discussed in the following section.

1.5 Catalytic decomposition of ozone in the aqueous phase: the role of activated carbon

Concerning wastewater treatment, the instability of ozone molecule is an advantage, as the formation of $HO^{\bullet}$ radicals transforms ozonation into an advanced oxidation process [20], enhancing its efficiency for the degradation of organic pollutants.

Many studies on ozone decomposition over catalyst surfaces in the gas phase have been carried out. These works are related to the destruction of ozone gas, e.g., at the outlet of an ozone contactor in a water treatment plant, due to the hazardous properties of that gas [20]. Different types of catalysts have been evaluated, including transition metal oxides and activated carbon. A common mechanism to explain the gas phase ozone catalytic decomposition over heterogeneous catalysts considers the adsorption of the ozone on the catalyst surface (S), and the formation of active oxygen adsorbed species (O-S), such as atomic oxygen, superoxide ($O_2^{-\bullet}$) or ozonide species ($O_3^{-\bullet}$), which further react with another ozone molecule to yield molecular oxygen. Such surface oxygenated groups were identified with the help of infrared studies.

$$O_3 + S \rightarrow O_3 - S \quad (1.10)$$

$$O_3 - S \rightarrow O - S + O_2 \quad (1.11)$$

$$O - S + O_3 \rightarrow S + 2O_2 \quad (1.12)$$

In contrast to the high number of studies on catalytic ozone decomposition in the gas phase, far few works deal with this subject in water [29, 30]. Among several materials, activated carbon was found to accelerate the decomposition of dissolved ozone, and the positive effect of the simultaneous use of ozone and activated carbon for removing pollutants from water has been the subject of various works, as reported in section 1.6.2.

1.5.1 Activated carbon properties

Due to its excellent adsorption properties, activated carbon is widely used in the fields of water and wastewater treatment. Moreover, activated carbons are largely used in heterogeneous catalysis because they can satisfy most of the desirable properties required for a suitable support, such as inertness, stability under reaction and regeneration conditions, adequate mechanical properties, high surface area and

porosity. Additionally, activated carbons are effective catalysts in a number of reactions [31]. The structure of activated carbons is generally described as a group of randomly cross-linked aromatic sheets and strips, with variable gaps of molecular dimensions between them, corresponding to the pores of the material (see Figure 1.6).

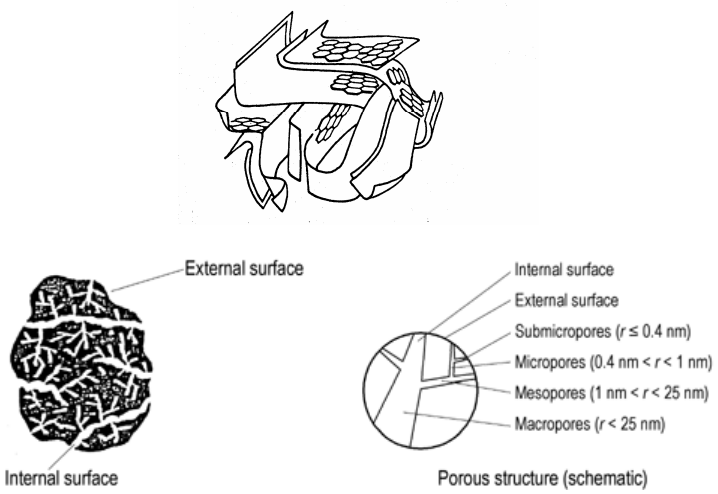

Figure 1.6 Schematic representation of the structure of activated carbon [32], and respective pore structure [33].

The adsorptive properties of activated carbon are determined not only by its porous structure but also by its surface chemical properties. The random ordering of defective aromatic sheets results in the existence of incompletely saturated valences and unpaired electrons, which influence the adsorption behaviour of the activated carbons. Usually, appreciable amounts of oxygen and hydrogen, in addition to other heteroatoms, such as chlorine, sulphur and nitrogen, are present in activated carbons [33]. Such elements may be present in the starting material and become chemically bond to the structure, in the form of functional groups, during calcination and activation steps. Among them, oxygen groups (see Figure 1.7), such as carboxyl, phenol, carbonyl, quinone, and lactone groups, are the most important in defining the surface chemical properties of activated carbons [32]. Alternatively, such groups may be introduced after preparation, via adequate post-treatments [34].

Carbon-oxygen surface groups can result from the oxidation with many oxidising gases (oxygen, ozone, nitrous oxide, nitric oxide, carbon dioxide, etc) and with oxidizing solutions (nitric acid, sodium hypochlorite, hydrogen peroxide, etc). On the other hand, heat treatments under inert atmosphere may be used to selectively remove some of those groups, leading to an increase in the basicity of the activated carbons [31].

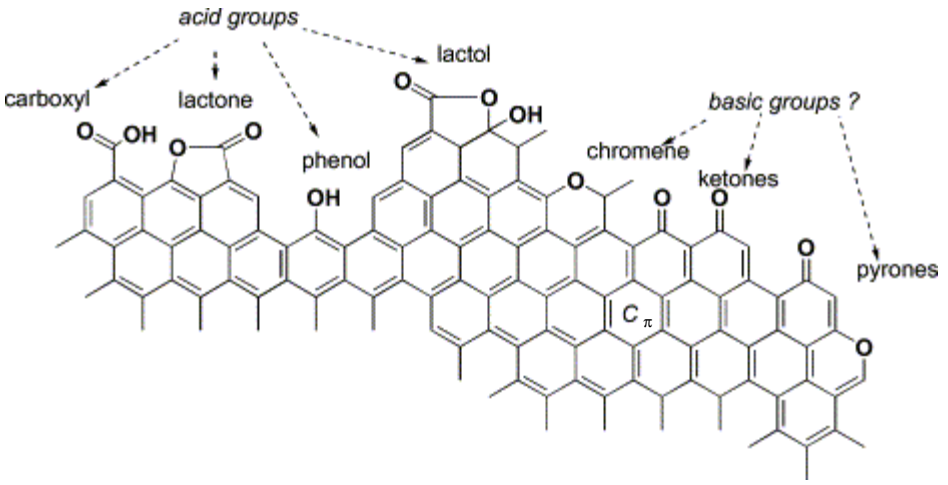

Figure 1.7 Proposed acid and basic functionalities on carbon surfaces [35].

Even though the basic character of the activated carbons has been associated with the presence of some oxygen-containing surface groups at the edges of carbon crystallites (e.g. chromene and pyrone-type groups), the main contribution to surface basicity is often attributed to the electron-rich oxygen-free Lewis basic sites on the carbon basal planes, i.e. within the graphene layers that constitute the carbon crystallites. In other words, carbon basicity is mainly associated with the absence of oxygenated functional groups predominantly of acidic nature, and to the consequent availability of delocalised π electrons on the carbon surface [36].

The surface oxygen complex content determines the charge of the surface, its hydrophobicity, and the electronic density of the graphene layers. Thus, when activated carbon is immersed in an aqueous solution, it develops a surface charge that results from the dissociation of surface groups or the adsorption of ions from solution [37], as illustrated in Figure 1.8.

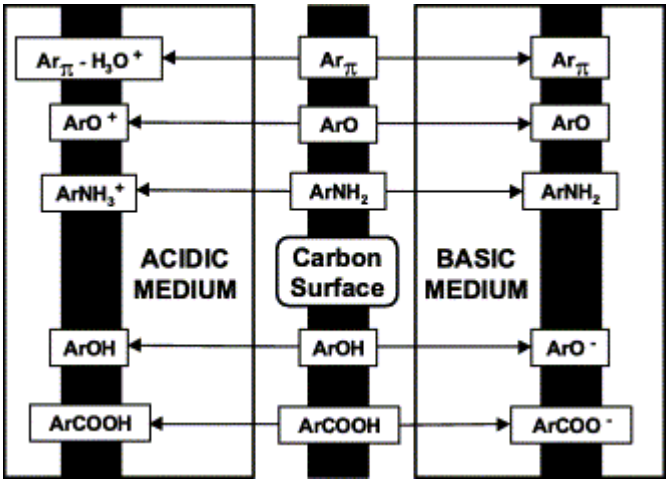

Figure 1.8 Schematic representation of the features of carbon surface chemistry in aqueous phase [38].

The surface charge will depend on the solution pH and the surface characteristics of the carbon. A negative charge (developed when pH_{pzc} < pH) results from the dissociation of surface oxygen complexes of acid character such as carboxyl and phenolic groups, which are acid sites of Brönsted type. The origin of the positive surface charge (occurs if pH_{pzc} > pH) is more uncertain because, in carbons without nitrogen functionalities, it can be due to surface oxygen complexes of basic character like pyrones or chromenes, or to the existence of electron-rich regions within the graphene layers acting as Lewis basic centres, which accept protons from the aqueous solution [37].

In summary, the chemical surface properties of carbon materials determine their performance as liquid-phase adsorbents, catalyst supports or catalysts. In addition to the quantity and quality of the surface functional groups, the nature of the free edge sites in the graphene layers and the unique amphoteric character of carbons are considered key issues [38]. In the next section the role of activated carbon regarding the decomposition of dissolved ozone is discussed.

1.5.2 Decomposition of ozone in the presence of activated carbon

Some authors have worked on the study of the decomposition of ozone in the presence of activated carbon in the aqueous phase, and a few attempts have been made to clarify the kinetics and mechanism of such process.

In 1998, Jans and Hoigné published an interesting work on the decomposition of aqueous ozone in the presence of activated carbon and carbon black [25]. Suspensions of activated carbon or carbon black were found to accelerate the depletion of ozone, acting as initiators for the radical type chain reaction that proceed in bulk solution, leading to the transformation of ozone into secondary oxidants, such as $HO^{\bullet}$. It was suggested that the catalytic decomposition of ozone was preceded by an adsorption step on the activated carbon surface. The pre-ozonation of activated carbon in aqueous solution did not affect its activity for decomposing ozone. These observations were in agreement with the findings of Dussert and Kovacic [39] who reported that long-time exposure of GAC filters to aqueous ozone did not significantly accelerate the oxidative degradation of the activated carbon. Thus, activated carbon can be considered relatively stable in ozonation operation in aqueous systems. Similar conclusions were later achieved by Guiza et al. [40] while studying the decomposition of dissolved ozone in the presence of activated carbon prepared from olive stones.

On the contrary, fairly different conclusions were achieved in the gaseous phase depletion of ozone on carbon materials, as both catalytic transformation of ozone and strong oxidation of the activated carbon occur [41]. This is due to the drastic conditions caused by high concentrations of gaseous ozone. According to Álvarez et al. [42], high surface area, volume of large pores, concentration of basic surface oxygenated groups, and metal content have been observed as desired GAC properties in order to achieve high rates of ozone conversion. All the used GAC samples exhibited gradual deactivation, which is likely due to the formation of acidic surface oxygenated groups. Effective reactivation of GAC could be achieved by thermal treatment at 850 ºC in nitrogen flow.

Beltrán et al. [43] presented a kinetic study of the heterogeneous catalytic ozone decomposition in water, in the presence of a commercial activated carbon. Carbon particle size, temperature and pH were amongst the variables investigated. The presence of activated carbon improved the decomposition of ozone in the pH range studied. Ozone decomposition was found to be pH dependent. In the view of the experimental results and information on the literature regarding the catalytic

decomposition of ozone in the gas phase, the following general mechanism was proposed [43], which involves both homogeneous and heterogeneous steps:

1. Homogeneous decomposition:

$$O_3 + HO^- \rightarrow HO_2^- + O_2 \quad (1.13)$$

$$O_3 + HO_2^- \rightarrow HO_2^{\bullet} + O_3^{-\bullet} \quad (1.14)$$

$$O_3 + In \rightarrow O_3^{-\bullet} + In^+ \quad (1.15)$$

$$HO_2^{\bullet} \leftrightarrow O_2^{-\bullet} + H^+ \quad (1.16)$$

2. Heterogeneous decomposition and surface reaction:

2 < pH < 6

$$O_3 + S \leftrightarrow O_3 - S \quad (1.17)$$

$$O_3 - S \leftrightarrow O - S + O_2 \quad (1.18)$$

$$O_3 + O - S \leftrightarrow S + 2O_2 \quad (1.19)$$

pH > 6

$$HO^- + S \leftrightarrow HO - S \quad (1.20)$$

$$O_3 + HO - S \leftrightarrow {}^{\bullet}O_3 - S + HO^{\bullet} \quad (1.21)$$

$${}^{\bullet}O_3 - S \leftrightarrow {}^{\bullet}O - S + O_2 \quad (1.22)$$

$$O_3 + {}^{\bullet}O - S \leftrightarrow O_2^{-\bullet} + S + O_2 \quad (1.23)$$

3. Homogeneous propagation and termination reactions:

$$O_3 + O_2^{-\bullet} \rightarrow O_3^{-\bullet} + O_2 \quad (1.24)$$

$$O_3^{-\bullet} + H^+ \rightarrow HO_3^{\bullet} \quad (1.25)$$

$$HO_3^{\bullet} \rightarrow HO^{\bullet} + O_2 \quad (1.26)$$

$$HO^{\bullet} + P \rightarrow \text{End products} \quad (1.27)$$

where S is the catalyst surface, In is an initiator of ozone decomposition, and P a scavenger of hydroxyl radicals. This mechanism highlights the role of activated carbon as an initiator of the ozone decomposition radical chain, leading to the formation of $HO^{\bullet}$ radicals that further react in the aqueous solution.

Based on previous findings [25], Sánchez-Polo et al. [44] investigated the efficiency of activated carbon to transform ozone into $HO^{\bullet}$, using *para*-chlorobenzoate (*p*-CBA) as a probe compound. Several operational parameters including carbon dose, carbon type and carbon pre-ozonation (both in the liquid and in the gas phase) were evaluated. The ozone decomposition rate constant was increased by the presence of activated carbon, and the ratio of concentrations $[HO^{\bullet}]/[O_3]$ was significantly enhanced. Both textural and chemical properties of the activated carbon were found to be governing factors for ozone transformation into $HO^{\bullet}$ radicals.

The decomposition of aqueous ozone in the presence of various lab-prepared and commercial granular activated carbons was also studied by Alvárez et al. [45]. From the experimental results it was deduced that GAC enhances the decomposition of ozone into $HO^{\bullet}$ radicals through the formation and further dissociation of H_2O_2. No direct relationship between textural properties of GAC and the rate of ozone decomposition was found. Basic and hydroxyl surface oxygen groups were found to favour the kinetics of the ozone decomposition process. Repeated use of GAC in ozonation experiments resulted in the modification of the surface chemistry of the carbon materials, due to the introduction of acid functional groups on the carbon surface, leading to the reduction of their activity for the decomposition of dissolved ozone.

A systematic study regarding the influence of surface chemistry and textural properties of activated carbon in the decomposition of dissolved ozone was carried out in this PhD work. This was one of the goals of this thesis and detailed discussion will be presented in chapter 2.

1.6 Catalytic ozonation for the degradation of organic compounds: general overview

Ozonation alone has been shown to achieve a limited mineralisation level concerning either the removal of micropollutants in drinking water treatment or the removal of refractory COD in industrial effluents. Consequently, various advanced

oxidation processes (AOPs) resultant from the combination of ozone with H_2O_2, UV radiation or Fenton's reagent have been investigated as potential methods for the elimination of organic compounds [27]. Such processes aim at the production of large amounts of $HO^{\bullet}$ radicals, which are non-selective oxidant species and react with a vast number of compounds at very high rates, comparatively to those of direct ozone reactions [22]. There are, however, some disadvantages limiting their application. AOPs are characterised by a strong dependence on the pH of the solution. The presence of radical scavengers in the water or wastewater to be treated can result in a significant reduction of the efficiency of contaminants removal.

Catalytic ozonation was found to be effective for the removal of several organic compounds from drinking water and wastewater, and intense research is being carried out on this subject. When dealing with catalytic ozonation, one should distinguish between homogeneous and heterogeneous processes.

The catalysts proposed for the process of homogeneous catalytic ozonation are usually transition metal ions (e.g. Fe, Mn, Co, Cd, Cu, Cr and Zn). Generally, two main processes can be considered when attempting to explain the mechanisms of homogeneous catalytic ozonation: ozone decomposition by means of active metal species in solution leading to the formation of free radicals, or formation of complexes between the metal ions and organic species followed by final oxidation reactions. Several factors such as the pH of the solution and reagents concentration can influence both the efficiency and the mechanism of homogeneous catalytic ozonation [46]. Despite the promising results presented in the literature, homogeneous catalytic ozonation has some drawbacks, mostly related to the difficulty in recovering the catalyst.

In water treatment, the high reactivity of ozone and the active surfaces of some materials can be used to increase the ozonation rate. In an attempt to improve the performance of advanced oxidation of water contaminants with ozone, several research groups focussed on the combined application of ozone and solid catalysts, and numerous papers have been published since the mid 1990s. The most common catalysts proposed for the process of heterogeneous catalytic ozonation are metal oxides such as MnO_2, TiO_2, Al_2O_3, ZnO and supported metal oxides (TiO_2/Al_2O_3, Fe_2O_3/Al_2O_3, Co_3O_4/Al_2O_3, MnO_2/TiO_2). Transition and noble metals supported on several oxides ($Cu\text{-}Al_2O_3$, Cu-TiO2, $Ru\text{-}CeO_2$, $Co\text{-}Al_2O_3$) have been investigated in ozonation reactions [27, 46]. Activated carbon by itself [47-49], metal oxides supported on activated carbon [50], metal-doped carbon aerogels [51] and, more

recently, Pt supported on carbon nanotubes [52] have also been tested in the ozonation of organic compounds.

The activity of such materials is frequently associated with their ability to catalytically decompose ozone leading to the formation of $HO^{\bullet}$ radicals. However, the results obtained in different studies suggest alternative ozonation mechanisms. Several authors reported a limited influence of radical scavengers on the efficiency of catalytic ozonation, which is an obvious evidence that not all the mechanisms involve the participation of hydroxyl radicals in solution as main oxidant species. It is probable that, under some conditions, adsorbed molecular ozone or other oxygenated surface species will be responsible for oxidation reactions. Accordingly, heterogeneous catalytic ozonation should not be perceived simply as an advanced oxidation process [46].

The efficiency of the catalytic ozonation process depends, to a great extent, on the catalyst and its surface properties, as well as on the pH of the solution, which influences the properties of surface active sites and ozone decomposition reactions in the aqueous phase. According to the literature, it is clear that a particular catalyst is active in certain conditions and for specific groups of organic molecules. The huge diversity of solid catalyst types, the variety of the surface properties, and the interactions between catalyst, ozone and organic molecule, make difficult the generalisation of the mechanisms involved. In the following sections a more detailed discussion on the ozonation catalysed by metal oxides, supported metal oxides, and activated carbon is presented.

1.6.1 Ozonation catalysed by metal oxides and supported metal oxides

Metal oxides represent one of the most important and widely employed classes of solid catalysts, either as active phases or supports. As previously mentioned, several reported studies have shown that metal oxides and supported metal oxides can be efficient for the catalytic ozonation of a vast range of organic contaminants.

Manganese oxides, especially MnO_2 are frequently cited as being highly effective in catalytic ozonation reactions. The activity of such materials has been evaluated in the ozonation of several organic compounds such as atrazine, oxalic acid, phenolic compounds, sulfosalicylic acid and propionic acid [46]. However, some

divergences on the proposed reaction mechanisms are present in the literature. Andreozzi et al. [53] have reported that the removal of oxalic acid increases when the ozonation is carried out at acid pH in the presence of MnO_2, due to the formation of a surface manganese-oxalate complex, which is easily oxidized by ozone. Ma and Graham [54] have shown that MnO_2, formed in situ from the ozonation of homogeneous Mn^{2+}, enhances significantly the removal of atrazine. The catalytic effect was attributed to the generation of $HO^{\bullet}$ radicals from the decomposition of ozone initiated on the surface of the catalyst. According to Beltrán et al. [47], the use of TiO_2 powder as a catalyst significantly improved the ozonation of oxalic acid, leading to total mineralisation. Based on literature information, the authors proposed a mechanism involving the adsorption and decomposition of ozone on the active centres of the catalysts and subsequent reaction with adsorbed organic species. Alumina (Al_2O_3), which is most commonly used as a catalyst support, has been shown to be active for the catalytic ozonation of natural organic matter [55] and refractory organic compounds [56]. In the latter work, the authors suggested that the dissolved ozone adsorbs on the catalyst surface and then decomposes, due to the presence of hydroxyl surface groups, leading to the formation of $HO^{\bullet}$. Those species would then oxidize the organic compounds either in the bulk solution or in the liquid-solid interface. According to that reasoning, the adsorption of the organics on the catalysts could be neglected.

More recently, nanosized ZnO materials were tested in the catalytic ozonation of *para*-chlorobenzoic acid [30] and 2,4,6-trichlorophenol [57]. In both works, ZnO was found to promote the formation of $HO^{\bullet}$ from the decomposition of ozone, leading to the enhanced degradation of the selected organic molecules.

Carbajo et al. [58] verified the activity and stability of perovskite catalysts ($LaTi_{0.5}Cu_{0.85}O_3$) in the ozonation of phenolic wastewater. The occurrence of surface reactions without the participation of $HO^{\bullet}$ in the liquid phase was suggested.

Natural mineral materials, such as brucite (magnesium hydroxide), have been presented as economical and feasible choices for the enhanced ozonation of nitrobenzene and aniline [59], or an azo dye [60].

Lim at al. [61] investigated the kinetics and mechanism of the decomposition of ozone and the removal of *p*-CBA in a soil slurry. The soil used was Jumunjin sand (Korea), composed mainly by SiO_2 and Al_2O_3, with trace amounts of Fe, Ti, Ca, Mg, K, Na and P oxides, and an organic matter content of 0.12% wt. The generation

of $HO^{\bullet}$ was demonstrated and it was verified that this was correlated with the metal oxides (MO) content, as well as with soil organic matter (SOM). Metal oxides in soil surface were considered to have relatively faster reaction rate with ozone and provide more favourable reactive sites to generate higher amount of $HO^{\bullet}$ than SOM. It was inferred that the radical reaction with the probe compound seemed to take place not only on the soil surface but also in the solid–liquid interface, as illustrated in Figure 1.9.

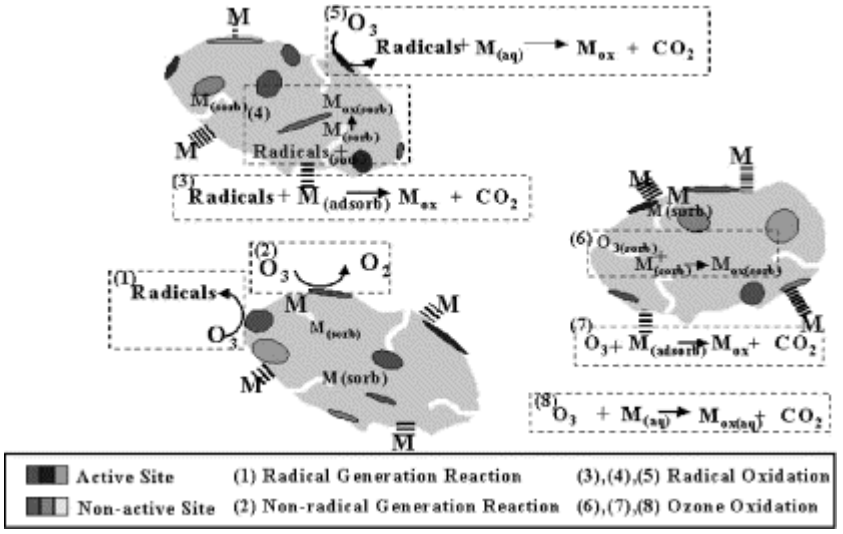

Figure 1.9 Conceptual scheme of catalytic reactions of ozone decomposition on soil surface and removal of organic contaminants (M stands for the organic compound) [61].

A volcanic sand constituted mainly by SiO_2, Al_2O_3 and Fe_2O_3, and containing measurable amounts of other metal oxides (Ti, Mg, Mn) was used by Valdés et al. [62] in the ozonation of benzothiazole. Experimental results showed that both benzothiazole removal and ozone self-decomposition were enhanced in the presence of the volcanic sand, especially at pH > pH_{pzc}, which, according to the authors, could be related to the ozone interaction with the strong Lewis acid sites present on the catalyst surface. The catalytic mechanism is supposed to involve both homogeneous (i.e. with the participation of $HO^{\bullet}$ radicals) and surface reactions.

Metal oxides can be immobilized on several supports such as clay, activated carbon or other metal oxides, being alumina, silica or TiO_2 the most commonly studied. Cooper and Burch [63] showed the significant influence of Al_2O_3, TiO_2/Al_2O_3 and

Fe_2O_3/Al_2O_3 on both the increase of aqueous ozone decomposition and on the removal of oxalic acid, chloroethanol and chlorophenol from water, when compared to single ozonation. Pure Al_2O_3 was highly active for the removal of oxalic acid. The modification of Al_2O_3 with TiO_2 or Fe_2O_3 increased the activity of the catalysts particularly in the cases of chloroethanol and chlorophenol. According to the mentioned authors, the nature of the organic molecule may be an important factor influencing the efficiency of catalytic ozonation.

Beltrán et al. [64] showed that transition metal oxides of Fe, Ti and Co supported on alumina could improve the mineralisation of phenol solutions comparatively to single ozonation. The system TiO_2/Al_2O_3 was further studied by the same authors [65] for the catalytic ozonation of oxalic acid at pH = 2.5. The combined use of ozone and this catalyst lead to 80% conversion of oxalic acid after 3h, which is a visible enhancement comparatively to the 2% removal obtained by single ozonation. The fact that ozone decomposition in the aqueous phase was not enhanced by the presence of the supported metal oxide, and the absence of any inhibitory effect of a radical scavenger in the process, lead the authors to suggest that the mineralisation of oxalic acid does involve neither surface bound oxygenated radicals nor $HO^{\bullet}$ radicals in the bulk. Adsorption of oxalic acid on the alumina and titania active sites, and subsequent direct reaction with molecular ozone following an Eley-Rideal mechanism, was proposed [65] (see equations 1.28 and 1.29, where B represents oxalic acid and S the alumina or titania active sites).

$$B + S \leftrightarrow B - S \tag{1.28}$$

$$O_3 + B - S \rightarrow 2CO_2 + H_2O + O_2 + S \tag{1.29}$$

Among transition metal oxides, cobalt based materials, which are extensively studied in oxidation reactions, have also been found to be potential catalysts for the ozonation of organic pollutants in water. The use of a Co_3O_4/Al_2O_3 (10% wt Co) catalysts prepared by impregnation has been observed to significantly enhance the ozonation rate of oxalic acid in water at low pH, leading to mineralisation [66]. The presence of tert-butanol, a well known $HO^{\bullet}$ radical scavenger, did not affect the oxalic acid removal rate. The occurrence of metal leaching is a major drawback of such catalyst, as it leads to decay in the activity. With the aim of improving the stability of Co/Al_2O_3 catalysts, Álvarez et al. [67] focussed on the preparation and structural characterization of low-loaded Co/Al_2O_3 catalysts (0.5 - 5% wt Co) and tested their performance on the ozonation of pyruvic acid. Differences in the

catalytic activity amongst the various Co-supported catalysts investigated were attributed to the different Co active phases (CoO, $CoAl_2O_4$, Co_3O_4) supported on the γ-Al_2O_3 surface. It was concluded that the sample containing Co_3O_4 as the main cobalt phase provided the most promising results.

Recently, Hu et al. [68] investigated the ozonation of an herbicide over cobalt oxide supported on mesoporous zirconia, which was found to be active for the respective degradation. Cobalt oxide was present mainly as Co_3O_4. The enhanced mineralisation of that pollutant achieved by catalytic ozonation was manly due to the presence of $HO^{\bullet}$, generated from the catalytic decomposition of ozone. The high dispersion of Co oxide and the multivalence oxidation states of cobalt (Co (II) and Co (III)) was suggested to be responsible for the catalytic activity. Such hypothesis was based on the decomposition mechanism of gaseous ozone on the surface of metal oxides [69], which is believed to consist mainly on redox steps: adsorption of ozone on the catalyst surface and decomposition to yield surface oxygen species and further desorption of the adsorbed intermediates.

When considering metal oxides as catalysts, both physical and chemical features must be taken in account. As for the physical properties, surface area, density, pore volume and pore size distribution, as well as mechanical strength are the main variables. The most important chemical properties are chemical stability and the presence of active surface sites. Metal oxides are used for both their acid-base and redox properties and constitute the largest family of catalysts in heterogeneous catalysis. The majority of oxide catalysts correspond to more or less complex transition metal oxides containing cations of variable oxidation state, which introduce redox properties, and also acid-base properties. Both characteristics are not independent since cations are Lewis acids, while lattice oxygen anions are basic, and hydroxyl groups can behave as acid or basic Brönsted sites [46]. Generally, metal oxides behave as amphoteric ion exchangers. Depending on the solution pH and on the corresponding pH_{pzc}, they can behave as cation or anion exchangers. The adsorption properties of metal oxides are of great importance when discussing the catalytic activity of heterogeneous catalysts as adsorption is often one of the stages of heterogeneous catalytic ozonation. Moreover, the great adsorption ability of metal oxides towards natural water constituents, such as inorganic ions (phosphates or carbonates), can cause permanent blockage of the catalysts active surface sites and the decrease of their catalytic activity. When the solution pH is lower than the pH_{pzc}, the surface of the metal oxide becomes

positively charged and favours the adsorption of anionic species. The adsorption of cations will proceed effectively at pH values higher than the catalyst pH_{pzc}, as its surface is negatively charged.

In summary, two main general mechanisms for the ozonation catalysed by metal oxides and supported metal oxides are proposed in the literature. One suggests the adsorption of ozone on the surface of the catalysts, and its further decomposition leading to the formation of surface bound oxygenated radicals, which are active oxidative species responsible for the oxidation of adsorbed organic molecules. Other mechanisms propose the adsorption of ozone and its decomposition, with the consequent generation of free $HO^{\bullet}$ radicals that promote oxidation reactions in the liquid phase or in the solid-liquid interface [46]. Oxidation proceeds stepwise through several oxidised intermediates, while radicals are continuously generated by the dissolved ozone that is transferred to the catalyst surface. The proposed mechanisms for the decomposition of ozone on the surface of metal oxide are generally based on those established for the catalytic decomposition of gaseous ozone. According to the literature [46], the adsorption of gaseous ozone on metal oxides may occur via physical adsorption, interaction with surface -OH groups, molecular adsorption or dissociative adsorption on Lewis acid, the latter leading to the formation of active oxygen species. Nevertheless, the nature of the catalyst sites responsible for the adsorption of ozone in the aqueous phase has not been clarified yet. Therefore, the phenomenon that rules adsorption and the fate of ozone on the surface of metal oxides is not fully understood.

1.6.2 Ozonation catalysed by activated carbon

Among the materials used to improve ozonation efficiency, activated carbon was shown to be a good alternative as it is believed to enhance the decomposition of dissolved ozone leading to the formation of highly oxidant species such as $HO^{\bullet}$ in solution and surface oxygenated active species.

The simultaneous use of ozone and activated carbon was first studied by McKay and MacAleavey [70] in the scope of the removal of colour from peat water. The authors observed that the removal of colour in the combined process was significantly improved when compared to single ozonation and single adsorption. A few years later, the combination of ozone and activated carbon in a single step was found to be beneficial for the oxidation of several chlorophenolic compounds [71].

By that time, a Netherlands company had developed Ecoclear® [17, 72], a continuous process based on the simultaneous use of ozone and a carbon based catalyst for the removal of colour and other refractory organic contaminants in wastewater, to be used as a final oxidation treatment (Figure 1.10).

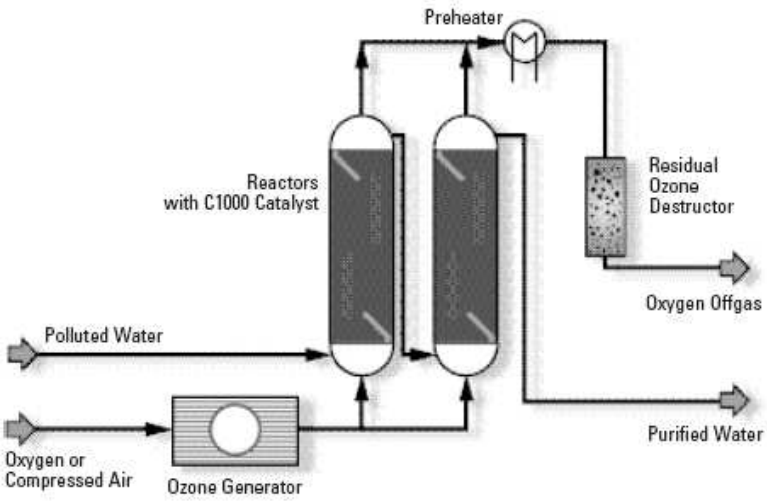

Figure 1.10 Flow scheme of a catalytic ozonation full-scale installation.

Based on experimental data and on the adsorptive properties of the catalyst, a mechanism assuming the simultaneous adsorption of ozone and organic molecules on the catalyst surface was postulated. Ozone would further decompose to surface bound oxygen radicals ($O^{-\bullet}$, $O_2^{-\bullet}$, and $O_3^{-\bullet}$), which would be responsible for the oxidation of adsorbed molecules [72].

Activated carbon can form oxygen radicals at the surface from molecular oxygen. As oxygen is a stable compound, the formation of such radicals will only take place at high temperatures. On the contrary, ozone is much less stable than oxygen, and, therefore, it can be transformed into radicals at ambient temperatures. The low influence of radical scavengers in the efficiency of the process led the authors to neglect the participation of $HO^{\bullet}$ in the oxidation mechanism [72].

Since the study from Jans and Hoigné [25] on the activated carbon catalytic decomposition of ozone into $HO^{\bullet}$ radicals, several papers related to the simultaneous use of ozone and activated carbon have been published and this subject is still under intense research. The large variety of compounds tested in this process includes small carboxylic acid, such as oxalic [73], pyruvic [74] and

succinic acids [75], and aromatic compounds such as naphtalenesulfonic acids [49, 76], phenolic compounds [77-79] and benzothiazole solutions [80]. The simultaneous use of ozone and activated carbon has been shown to be a promising method for the mineralisation of dye solutions [81] and for the treatment of textile wastewater [48, 82, 83], especially when used as a final oxidation treatment for biotreated effluents.

In many of these studies, the objective has been mainly focussed on the analysis of the effect of different variables on the ozonation rate, ozone uptake or process efficiency. Others have focussed on the kinetics of the ozonation process. In some works attention was paid to the influence of the properties of the activated carbon, but no systematic work was presented. Several approaches have been made to the reaction mechanisms involved.

Rivera-Utrilla and Sánchez-Polo [49, 76] studied the ozonation of 1,3,6-naphtalenetrisulphonic acid in the presence of several commercial activated carbons and found correlations between ozonation rates and activated carbon basicity and porosity. The catalytic effect of that process was attributed to an enhanced decomposition of ozone on the basic sites of the activated carbon, which include the delocalized π electrons of the carbon basal planes, and oxygenated surface groups of basic nature (chromene and pyrone functional groups).

The catalytic decomposition of ozone towards the formation of $HO^{\bullet}$ in solution is generally accepted by several authors as one of the steps of the ozonation promoted by activated carbon. According to the literature, the generation of $HO^{\bullet}$ is initiated by the adsorption and decomposition of ozone on the surface of the activated carbon or by the formation of hydrogen peroxide.

In summary, the catalytic ozonation of organic compounds in the presence of activated carbon may involve both homogeneous and heterogeneous reactions. According to the results presented in the literature, activated carbon plays different roles in the catalytic process. It is able to initiate and promote the decomposition of ozone on its surface leading to the formation of surface oxygenated radicals and/or to the generation of $HO^{\bullet}$ in solution. Therefore, the oxidation of the organic compounds may occur either on the activated carbon surface or in the bulk.

Due to the fact that activated carbon surface properties may be modified during the ozonation process, some authors suggested that these process should not be catalogued as a catalytic ozonation process [78]. However, no appreciable

differences were observed in the activity of activated carbon for the catalytic ozonation of pyruvic acid after three consecutive utilisations [74]. Even though no characterization of used activated carbon was presented, these authors concluded that activated carbon was relatively stable in ozonation reactions. In this scope, there seems to be no reason for not considering activated carbon as an ozonation catalyst, which is naturally subjected to a possible deactivation.

1.7 Objectives and thesis outline

A few years ago, during my Master thesis [84], I started working on the ozonation of commercial textile dyes in the presence of activated carbon [81], with the main goal of studying the application of the combined use of ozone and activated carbon to the final treatment of textile effluents. Based on the experimental results obtained, it was concluded that activated carbon catalysed the ozonation of the dyes leading to an enhanced removal of the total organic carbon (TOC) of the solutions. The adsorption contribution could not be neglected and the surface chemistry of the activated carbon appeared to play an important role in the reaction mechanism. Those preliminary results were the main driving force for the work presented in this thesis. Catalytic decomposition of dissolved ozone was thought to be one of the steps responsible for the enhanced results obtained in the ozonation in the presence of activated carbon. Therefore, this work started with the investigation of the role of activated carbon and the influence of both textural and chemical properties of that material in the decomposition of dissolved ozone. Subsequently, the catalytic ozonation of several organic model compounds, as well as commercial dyes and textile effluents, was studied in a semi-continuous lab-scale reactor.

This thesis is organized in six parts. The main core of the text is composed of Parts II, III, IV and V.

Part II consists in a systematic study of the influence of both textural and surface chemical properties of activated carbon in the decomposition of ozone in the aqueous phase.

Part III is dedicated to the ozonation of several organic model compounds (aniline, sulfanilic acid, benzenesulfonic acid, oxalic and oxamic acids) in the presence of activated carbons with different surface chemistries. In this section, the influence of

the surface chemical properties of activated carbon was evaluated, and possible reaction mechanisms were presented.

Part IV is related to the application of metal oxides as ozonation catalysts for the mineralisation of model organic compounds. The first chapter of this section consists in the preparation, characterization and evaluation of several metal oxides and metal oxides supported on activated carbon for the catalytic ozonation of selected organic compounds. The following chapters of this section are dedicated to the development of cerium oxide catalysts for the catalytic ozonation of carboxylic and aromatic acids. In this part of the work, a composite material of cerium oxide and activated carbon was successfully prepared and found to be a highly effective ozonation catalyst.

The catalysts with best performances were tested in the degradation of three commercial textile dyes. In addition, two effluents generated in the textile industry, collected before or after biological treatment, were selected as case studies, in order to evaluate the performance of the selected catalytic systems. The main results are presented in Part V.

The final section, Part VI, summarises and integrates the main conclusions withdrawn from this work. Finally some suggestions for forthcoming work are presented.

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Part II

Ozone Decomposition Catalysed by Activated Carbon

Activated carbon was found to enhance the mineralisation of organic compounds in ozonation reactions. Even though the reaction mechanism of the ozonation of organic compounds in the presence of activated carbon is not fully understood, it is suggested by several authors to involve the decomposition of ozone on the surface of the activated carbon leading to the formation of active oxygen species, which participate in the oxidation of the organic compounds. Due to their heterogeneous nature, both textural and chemical properties of activated carbons may influence the catalytic decomposition of ozone in the aqueous phase.

This part of the thesis is dedicated to the systematic study of the influence of the surface chemistry and textural properties of activated carbon in the decomposition of dissolved ozone. For this purpose, two series of modified activated carbons differing, either in the surface chemistry or in their textural properties, were prepared starting from the same commercial sample. The influences of variables such as solution pH, temperature, amount of activated carbon, and particle size were also assessed.

2 Ozone Decomposition in Water Catalysed by Activated Carbon: Influence of Chemical and Textural Properties[1,2]

The decomposition of ozone in water at different solution pH in the absence or presence of activated carbons with different surface chemical and textural properties was investigated. Activated carbon acts as a catalyst in the decomposition of ozone into radical species, significantly accelerating this process. Homogeneous and heterogeneous decomposition of ozone were described by second-order kinetic models. In general, both homogeneous and heterogeneous ozone decomposition rates increase with solution pH. Textural and surface chemical features of the activated carbon play a role in the catalytic decomposition of ozone. Heterogeneous ozone decomposition is enhanced by activated carbon with high surface area and basicity. Despite the mild oxidation undergone by the activated carbon samples during ozonation, no strong deactivation occurs.

2.1 Introduction

Ozone is one of the most powerful oxidant agents available. It is widely used for drinking water disinfection and for the oxidation of pollutants in industrial wastewater. Ozone is unstable in water and decomposes into radicals such as $HO^{\bullet}$, which are the strongest oxidants in water. For different applications of ozone technology, those species are of distinct importance. While disinfection occurs primarily through molecular ozone attack, oxidation processes occur mainly via an indirect pathway, involving various highly reactive radical species resultant from ozone decomposition [1]. Therefore, the decomposition of ozone in water plays an important role in the application of ozonation processes in the liquid phase.

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[1] Based on PCC Faria, JJM Órfão, MFR Pereira, Ind Eng Chem Res 45 (2006) 2715-2721.

[2] Additional data presented in Appendix B.

Ozone self-decomposition in water is highly influenced by temperature, pH, and presence of organic and inorganic species, and this subject has been studied by many authors over decades. Gurol and Singer [2] presented a review of several kinetic studies of ozone decomposition in water. From the works listed in the mentioned paper, it can be concluded that there is some disagreement among the results obtained. The most common divergence among researchers is about the order of the decomposition reaction, which generally varies between 1 and 2. Most of the investigations are not supported by reaction mechanisms, and the experimental conditions vary greatly [3]. Nonetheless, all the authors agree that the decomposition of ozone in water is catalysed by the hydroxide ion. According to Staehelin and Hoigné [4], the initiation of ozone decomposition can be highly accelerated by increasing the pH or by the addition of hydrogen peroxide.

To enhance the decomposition of ozone and, consequently, the efficiency of ozone-based oxidation processes, other methods combining ozone with homogeneous or heterogeneous catalysts, with or without metallic phases, have been investigated [5, 6]. These processes are based on the enhanced transformation of ozone into $HO^{\bullet}$ radicals, which have a high reactivity with most organic and inorganic pollutants, and play an important role in the mineralisation of refractory organic compounds [7].

Among these processes, the combination of ozone and activated carbon in a single step was found to be an attractive alternative to the treatment of wastewaters containing dyes or other organic contaminants [7-12], but only a few papers focused on the decomposition of ozone in aqueous solutions in the presence of activated carbon [13-16]. The mentioned studies report that activated carbon accelerates the decomposition of ozone, leading to the formation of several radical species, including the $HO^{\bullet}$ radicals. Jans and Hoigné [14] concluded that suspensions of activated carbon and carbon black can initiate the radical-type chain reactions that proceed in bulk solution and accelerate the transformation of ozone into secondary oxidants, such as $HO^{\bullet}$ radicals. Similar conclusions have been reported by Béltran et al. [13]. These authors studied the homogeneous and heterogeneous ozone decomposition at different pH and proposed a kinetic model based on the Langmuir-Hinshelwood type mechanism for the heterogeneous surface reaction. In another study, Guiza et al. [15] analysed the effect of the addition of granular activated carbon, produced from olive stones, on the rate of ozone decomposition in aqueous solutions containing radical promoter and inhibitor compounds. Among

other factors, they concluded that the ozone decomposition kinetics is enhanced when the activated carbon specific area increases. More recently, Sánchez-Polo et al. [16], investigated the activity of activated carbon for the transformation of ozone into $HO^{\bullet}$ radicals, on the basis of different operational parameters, using *para*-chlorobenzoate (*p*-CBA) as a probe compound. According to this work, chemical and textural properties of the activated carbon are the governing factors for ozone transformation into $HO^{\bullet}$ radicals.

The objective of the present work is to study systematically the influence of the surface chemistry and textural properties of the activated carbon in the catalytic decomposition of ozone in aqueous solution. To achieve this main goal, the decomposition of ozone in water was investigated at different solution pH in the presence of two series of modified activated carbons differing either in the surface chemical properties or in their textural characteristics.

2.2 Experimental

2.2.1 Preparation and characterization of the activated carbon samples

A Norit GAC 1240 PLUS activated carbon (sample AC_0) was used as the starting material for the preparation of two series of materials: a set of activated carbon samples with similar texture but different chemical surface properties, and another one with different textural properties and similar surface chemistry. For the first case, samples were prepared by oxidation with HNO_3 in the liquid phase and thermal treatment under H_2. Oxidation with HNO_3 was performed using a 100 cm^3 Soxhlet extraction apparatus containing 9 g of activated carbon, connected to a boiling flask and to a condenser. In each run, 200 cm^3 of HNO_3 6 M were introduced into a 250 cm^3 Pyrex round-bottom flask and heated to boiling temperature with a heating mantle. The reflux was stopped after 3 h. The activated carbon was washed with distilled water to neutral pH, dried in an air convection oven at 110 ºC for 24 h, and stored in a desiccator for later use (sample $ACHNO_3$). This sample was used as the starting material for the thermal treatment described below, since it is important that the starting material presents a large amount of surface groups in order to produce activated carbons with a high basic character [17]. About 3 g of sample $ACHNO_3$ were placed in a fused-silica tubular reactor,

heated to 700 ºC at 10 ºC/min under a flow of H_2 (50 cm^3/min, measured at room T and P), and kept at this temperature for 1 h. The sample was cooled to room temperature under the same atmosphere, collected, and stored in a desiccator (sample ACH_2).

The second series was prepared by catalytic gasification of sample AC_0, previously impregnated with 3.5% of Co, at 900 ºC under CO_2 during different time intervals (4 – 8 h) [18]. The samples were labelled as follows: ACgxh, where x is the time of gasification. After gasification, these carbon materials were washed with HCl 0.05 M to remove the impregnated cobalt, then washed with distilled water until a neutral pH was reached, and finally dried in the oven at 100 ºC. Since the purpose was to study the influence of the textural properties in the ozone decomposition reaction, all the materials were subsequently treated under inert atmosphere in order to have similar surface chemical properties. The samples were heated up to 900 ºC at 10 ºC/min under a flow of N_2 (100 cm^3/min measured at room T and P) and kept at this temperature for 1 h, to decompose the oxygen-containing surface groups. For comparative purposes, sample AC_0 was submitted to the same thermal treatment, originating sample ACN_2. With this procedure, materials differing only in the textural properties were obtained. All treatments were performed on the unground materials (particle size = 0.42 - 2 mm).

The textural characterization of the materials was based on the N_2 adsorption isotherms, determined at 77 K with a Coulter Omnisorp 100 CX apparatus. The micropore volumes (V_{micro}) and mesopore surface areas (S_{meso}) were calculated by the *t*-method using the standard isotherm proposed by Rodríguez-Reinoso et al. [19]. The adsorption data were also analysed with the Dubinin equation. In all cases, a type IV deviation was noticed [20]; therefore, two micropore structures were taken into account, and the corresponding volumes, W_{01} and W_{02}, were calculated [20]. The Stoeckli equation [21] was used to estimate the average micropore width of the smaller pores (L_1), using a value of 0.32 for the affinity coefficient of nitrogen.

The surface chemistry of the activated carbon samples was fully characterised by the determination of acidity, basicity and pH_{pzc}; temperature-programmed desorption (TPD); proximate analyses, as described elsewhere [22]; and X-ray photoelectron spectroscopy (XPS), with a VG Scientific ESCALAB 200A spectrometer using nonmonochromatized Mg Kα radiation (1253.6 eV).

2.2.2 Ozone decomposition in the aqueous phase

The ozone decomposition experiments were carried out in a laboratory-scale reactor (ca.1 L) equipped with mechanical agitation and a recirculation jacket (see Appendix A). Ozone was produced from pure oxygen in a BMT 802X ozone generator. The concentration of the ozone in the gaseous phase was monitored with a BMT 964 ozone analyser. Ozone in the gas phase leaving the reactor was removed in a series of gas-washing bottles filled with iodide potassium (KI) solution. Homogeneous and heterogeneous ozone decomposition experiments were performed at 25 ºC, controlled by a thermostatic bath, and different solution pH (3, 5, 7 and 9). In each experiment, 700 mL of 0.01 M phosphate buffer solution (NaH_2PO_4/Na_2HPO_4) was introduced in the reactor. Gaseous ozone was fed to the reactor for approximately 30 min to saturate the solution with ozone and, at the same time, remove any trace of organic matter that could further affect the ozone stability. The initial concentration of dissolved ozone varies approximately between 4 mg/L (pH = 9) and 15 mg/L (pH = 3). Prior to each heterogeneous ozone decomposition experiment, 140 mg of activated carbon (particle size = 0.1 - 0.3 mm) was put inside the reactor. To keep the reactor content perfectly mixed, the agitation was maintained constant at 300 rpm. Samples were taken regularly for quantification of dissolved ozone by the indigo method [23]. After each experiment, the activated carbon samples were withdrawn, dried at 100 ºC, and kept in a desiccator for further characterization.

2.3 Results and discussion

2.3.1 Characterization of the activated carbon samples

The physical properties of the materials modified by chemical and thermal treatments and by gasification, as well as those of the starting activated carbon, were obtained from the analysis of the N_2 adsorption isotherms at 77 K. Table 2.1 summarises the results.

Table 2.1 Textural characterization of the AC samples.

Sample	S_{BET} (m^2/g)	S_{meso} (m^2/g)	V_{micro} (cm^3/g)	W_{01} (cm^3/g)	W_{02} (cm^3/g)	L_1 (nm)
AC_0	909	100	0.332	0.305	0.035	1.1
$ACHNO_3$	827	88	0.304	0.276	0.035	0.8
ACH_2	896	92	0.334	0.297	0.044	1.0
ACN_2	951	103	0.351	0.315	0.044	0.9
ACg4h	1381	121	0.539	0.440	0.108	1.3
ACg6h	1564	177	0.624	0.462	0.169	1.5
ACg8h	1803	206	0.760	0.504	0.261	1.5

Liquid-phase oxidations and thermal treatments have been reported not to significantly change the textural properties of the activated carbon, when performed under controlled experimental conditions [24]. In fact, analysis of the characterization results obtained for samples AC_0, $ACHNO_3$, ACH_2, and ACN_2 shows that no major differences in the textural properties of these materials were observed.

For the second group of samples, it is observed that the Brunauer-Emmett-Teller (BET) surface area increases substantially with the extent of the gasification, as expected. The same occurs with the surface area of mesopores, the volume of micropores, and the average width of the smaller micropores. In fact, both the area of mesopores and the volume of micropores double from ACN_2 to ACg8h.

The acidity and basicity of the samples are shown in Table 2.2, and the pH_{pzc} values, determined by drift tests, are presented in Figure 2.1 (The pH at which the curve crosses the line $pH_{initial} = pH_{final}$ is taken as the point of zero charge, pH_{pzc} [25]). According to this figure, sample $ACHNO_3$ has a pH_{pzc} of ca. 3; the pH_{pzc} of sample AC_0 lies between 8 and 9, while samples ACH_2 and ACN_2 have a pH_{pzc} between 10 and 11.

Table 2.2 Acidity and basicity of the AC samples.

Sample	Acidity ($\mu mol/g_{AC}$)	Basicity ($\mu mol/g_{AC}$)
AC_0	211	352
$ACHNO_3$	1003	77
ACH_2	102	460
ACN_2	116	485

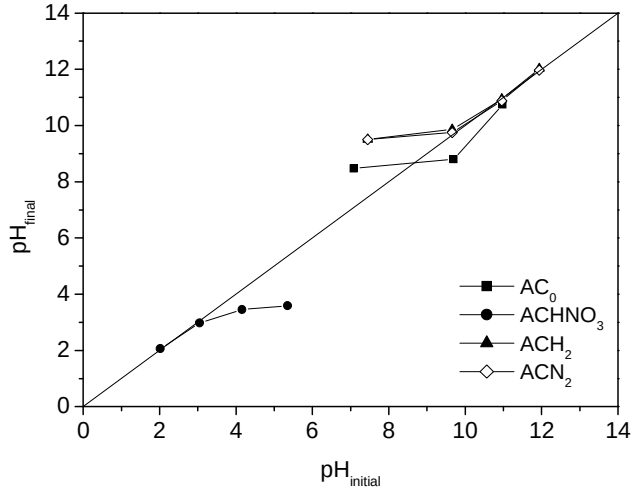

Figure 2.1 pH_{pzc} of the AC samples.

As expected, the surface acidity increased for sample $ACHNO_3$ because of the introduction of several oxygen-containing functional groups, namely, carboxylic acids, whereas the surface basicity decreased. Accordingly, this treatment yields samples with low pH_{pzc}. On the other hand, samples ACH_2 and ACN_2 have the highest basic character, as a consequence of the removal of such groups. Proximate analysis results (see Appendix B) revealed that oxidation with HNO_3 leads to a substantial increase in volatiles content. This is related to the amount of oxygen-containing groups introduced on the activated carbon surface. Thermal treatment

under H_2 and N_2 resulted in the removal of an important fraction of the oxygen groups from the surface of the carbon, which led to a decrease in the volatiles content. Samples ACg4h, ACg6h, and ACg8h have a basic character, similar to sample ACN_2, since they were submitted to the same thermal treatment. Figure 2.2 shows the TPD spectra of the activated carbon as received and after the oxidative and thermal treatments. Surface oxygen groups on carbon materials decompose upon heating, releasing CO and CO_2 at different temperatures. According to this, it is possible to identify and estimate the amount of oxygenated groups on a given carbon by TPD experiments. It was reported [24] that CO_2 peaks result from the decomposition of carboxylic acids at low temperatures or from that of lactones at high temperatures; anhydrides originate both CO and CO_2; and groups such as phenols, carbonyls, ethers, and quinones originate CO peaks.

The results clearly show that sample $ACHNO_3$ has the highest amount of surface oxygen-containing groups. On the other hand, thermal treatments at high temperature under H_2 or N_2 flow originate materials with a low content of oxygen-containing groups. As can be seen in the TPD spectra of samples ACH_2 and ACN_2, the CO_2 releasing groups have been removed almost completely, but some groups releasing CO at high temperatures still remain on the carbon surface. These are presumed to be part of the carbonyl groups that have not been removed by the thermal treatment and of the basic groups (such as pyrones and chromenes) which decompose at higher temperatures [26]. Thermally treated samples have a basic character which is due to these types of oxygen-containing groups and mainly to the electron-rich oxygen-free sites located on the carbon basal planes [27].

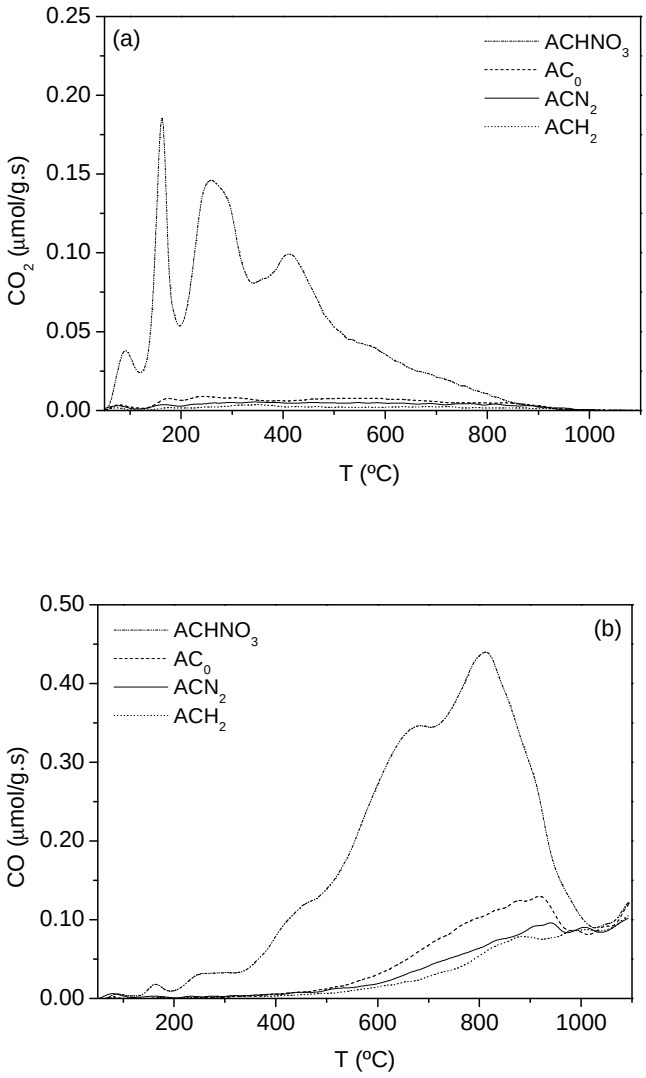

Figure 2.2 TPD spectra for samples AC_0, ACH_2, ACN_2 and $ACHNO_3$: (a) CO_2 evolution and (b) CO evolution (heating from room temperature to 1100 ºC at 5 ºC/min under 25 Ncm^3/min of He).

2.3.2 Ozone decomposition in aqueous solution

The decomposition of ozone in aqueous solution was studied in a laboratory reactor on the basis of several experiments under different solution pH values, in the absence or presence of activated carbons differing in their chemical and textural properties. The influences of temperature, amount of activated carbon, and particle size were also assessed (see Appendix B).

2.3.2.1 Homogeneous ozone decomposition

Figure 2.3 shows the evolution of normalised ozone concentration at different values of pH. It is clear that the decomposition rate increases with pH. This observation is consistent with the well-known mechanism for the ozone decomposition in the aqueous phase [4], since HO^- is one of the species responsible for the initiation step of the reaction mechanism.

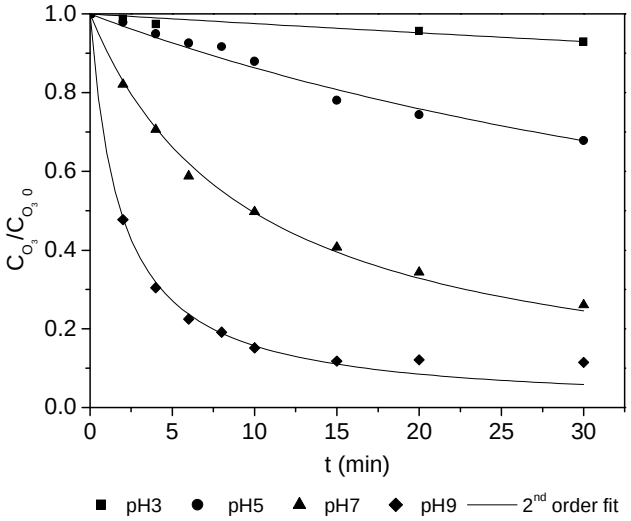

Figure 2.3 Influence of the pH on the homogeneous decomposition of ozone at 25ºC ($C_{O_3 0}$ = 15, 14, 10 and 3.8 mg/L, at pH = 3, 5, 7 and 9 respectively).

The homogeneous decomposition of ozone in the aqueous phase has been studied for years. However, both the order of the decomposition reaction and the magnitude of the reaction rate constant are still objects of discussion [2, 3, 13]. In the present

work, experimental data were analysed considering first-, 3/2- and second-order kinetic models. The second-order fit was significantly better in the entire range of studied pH. According to the second-order kinetic model, the evolution of ozone concentration is described by the following equation,

$$-\frac{dC_{O_3}}{dt} = k_{Homog} C_{O_3}^2 \qquad (2.1)$$

where k_{Homog} ($L.mg^{-1}.min^{-1}$) represents the second-order apparent rate constant and C_{O_3} (mg/L) is the concentration of dissolved ozone in each instant. Integration of equation (2.1), considering $C_{O_3} = C_{O_3 0}$ when $t = 0$, leads to:

$$\frac{C_{O_3}}{C_{O_3 0}} = \frac{1}{1 + k_{Homog} C_{O_3 0} t} \qquad (2.2)$$

Apparent second-order rate constant values, obtained from non-linear fitting, are listed in Table 2.3. It should be stressed out that the simple kinetic model presented was used to allow a quantitative comparison of the different materials. The detailed kinetic study of the decomposition of ozone in the presence of activated carbon was not the main goal of this work.

2.3.2.2 Heterogeneous ozone decomposition: influence of the surface chemical and textural properties of the activated carbon

According to a few studies published in the literature [13-16], the presence of activated carbon accelerates the decomposition of ozone in the aqueous phase. In this paper, a systematic approach is proposed in order to understand the role of the activated carbon properties in this process.

The decomposition of ozone in the presence of activated carbons with similar textural properties and increasing surface basicity was considered in the first place. These experiments were carried out at several pH conditions (3, 5, 7, and 9). The results obtained for pH 3 and pH 7 are presented in Figure 2.4 and Figure 2.5, respectively (see Appendix B for additional data). It is observed that the presence of activated carbon accelerates the decomposition of ozone. Similar to what happened with the results from homogeneous decomposition, experimental data for heterogeneous catalytic runs are fitted by a second-order kinetic model.

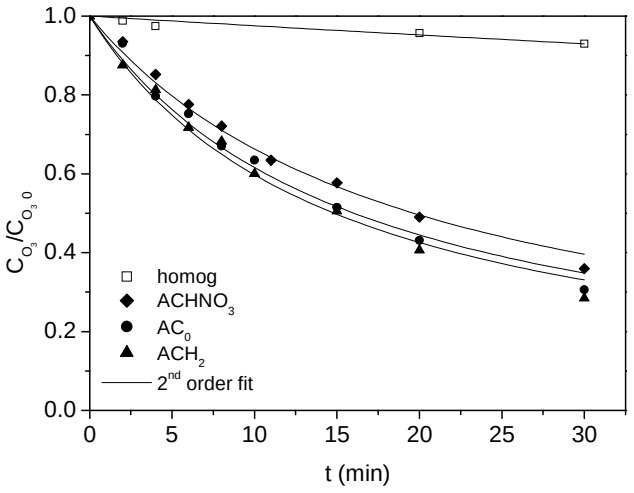

Figure 2.4 Influence of AC surface chemistry on the heterogeneous decomposition of ozone at pH 3.

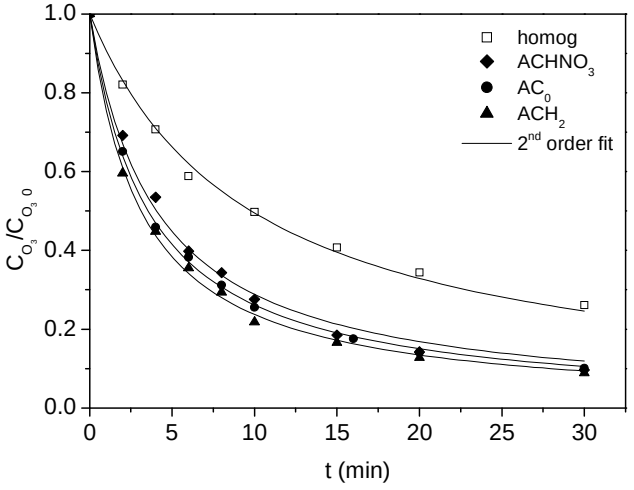

Figure 2.5 Influence of AC surface chemistry on the heterogeneous decomposition of ozone at pH 7.

In the presence of activated carbon, both homogeneous and heterogeneous decomposition of ozone occur. Thus, the ozone decomposition rate is the sum of two contributions. Therefore,

$$-\frac{dC_{O_3}}{dt} = (k_{Homog} + k_{Het})C_{O_3}^2 \qquad (2.3)$$

where k_{Homog} and k_{Het} ($L.mg^{-1}.min^{-1}$) represent second-order apparent rate constants for the homogeneous and heterogeneous decomposition, respectively, and C_{O_3} (mg/L) is the concentration of dissolved ozone in each instant. Integration of equation (2.3), considering $C_{O_3} = C_{O_3 0}$ when $t = 0$, leads to:

$$\frac{C_{O_3}}{C_{O_3 0}} = \frac{1}{1 + (k_{Homog} + k_{Het})C_{O_3 0}t} \qquad (2.4)$$

Apparent second-order rate constant values obtained from non-linear fitting according to equation (2.4) are listed in Table 2.3. For the fitting procedure, the values of k_{Homog}, previously calculated, were fixed.

Table 2.3 Apparent second-order rate constants for homogeneous and heterogeneous ozone decomposition.

pH	k_{Homog} x 10^3 (L mg^{-1} min^{-1})	k_{Het} x 10^3 (L mg^{-1} min^{-1})			$\frac{k_{Het}(AC_0)}{k_{Homog}}$
		$ACHNO_3$	AC_0	ACH_2	
3	0.17 ± 0.02	3.3 ± 0.1	4.1 ± 0.2	4.3 ± 0.2	24 ± 4
5	1.13 ± 0.05	2.72 ± 0.07	5.1 ± 0.2	5.9 ± 0.5	4.5 ± 0.4
7	9.7 ± 0.3	13.7 ± 0.9	18.6 ± 0.4	19.7 ± 0.7	1.9 ± 0.1
9	141 ± 8	49 ± 12	32 ± 9	83 ± 9	0.23 ± 0.08

Generally, the heterogeneous rate constant increases with pH, but the relative effect (k_{Het}/k_{Homog}) is more pronounced for lower pH, where the contribution of homogeneous decomposition is less significant. The ratio between k_{Het} for sample AC_0 and k_{Homog} is shown in Table 2.3, as an example. In general, it was observed that the trend of the catalytic activity for the decomposition of ozone is ACH_2 > AC_0 > $ACHNO_3$, following the decrease of basicity, according to other authors [16].

The mechanism of homogeneous ozone decomposition is well-established. On the contrary, the decomposition of ozone on the surface of activated carbons in aqueous phase is still an object of investigation, as mentioned before. Some authors suggested that the catalytic decomposition of ozone involves the adsorption of ozone and HO^- on the surface of activated carbon [13, 14]. Basic activated carbons are characterised by having a low content of surface oxygenated electron-withdrawing groups and by the existence of delocalized π electrons in the basal planes of the activated carbon [27]; therefore, the electron density on the surface is high when compared to that of acid activated carbons. Thus, basic activated carbons favour the adsorption step of ozone molecules as a result of the dispersive interactions between those electrons and ozone molecules. On the other hand, they act as an electron source favouring the reduction of ozone molecules, which have the ability to withdraw electrons from a given source (electrophilic behaviour). Consequently, basic activated carbons have a higher catalytic activity for ozone decomposition.

As mentioned before, the pH of the solution has a remarkable effect on the decomposition of ozone catalysed by activated carbon. Because of the amphoteric nature of the activated carbon, its surface might be positively or negatively charged, depending on the aqueous solution pH. When the pH_{pzc} of the activated carbon is higher than the pH of the solution, the surface of the material becomes positively charged, enhancing the attraction of hydroxide ions. On the other hand, if the pH_{pzc} of the carbon is lower than the solution pH, then repulsive electrostatic interactions between the activated carbon surface and HO^- ions will prevail. Finally, when the pH of the solution equals the pH_{pzc} of the activated carbon, the surface becomes neutral. Thus, electrostatic interactions may also play an important role in the catalytic decomposition of ozone. Several authors have to referred the positive effect of the hydroxide ions in both homogeneous and heterogeneous ozone decomposition [2-4, 13, 14]. Those findings are in agreement with the values obtained in the present work for the heterogeneous ozone decomposition apparent rate constant, which generally increases with the pH. Nevertheless, there is an exception to this generic trend, corresponding to the results obtained with the acid activated carbon when pH is raised from 3 to 5. According to Figure 2.1, the pH_{pzc} of sample $ACHNO_3$ is ca. 3, which means that the surface of this activated carbon sample is neutral at pH 3 and becomes negatively charged at pH 5. Therefore, the interaction of the activated carbon with HO^- ions is not favoured at pH 5. This

discrepancy may be explained on the basis of the previous reasoning about the influence of the electrostatic interactions. Furthermore, the increase of k_{Het} from pH 7 to pH 9 is significantly higher for sample ACH_2. Once again, this might be clarified by taking into account electrostatic interactions. At pH 9, ACH_2 is the only sample with a positively charged surface (see Figure 2.1), hence enhancing the interaction between the activated carbon surface and the hydroxide ions. As a result, the heterogeneous decomposition of ozone is particularly improved.

The decomposition of aqueous ozone was also studied in the presence of activated carbon samples with similar surface chemical properties and different textures. Samples ACN_2, ACg4h, ACg6h and ACg8h have different degrees of gasification which result in different textural properties. All the samples were submitted to the same thermal treatment at high temperature; as a result, they have similar surface chemical properties. According to the textural characterization, these samples have increasing specific surface areas and micropore volumes. Figure 2.6 shows the evolution of the dimensionless ozone concentration for each of the above mentioned activated carbon samples at pH 7. The decomposition of ozone increases with the gasification degree of the samples. In all cases, experimental data is well fitted by the second-order model previously described.

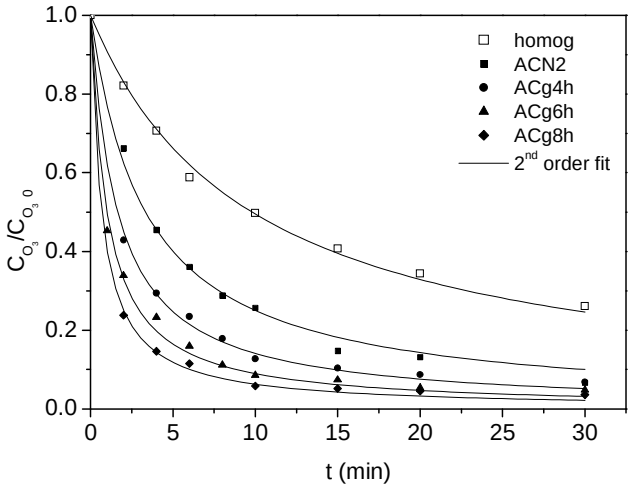

Figure 2.6 Influence of AC textural properties on the heterogeneous decomposition of ozone at pH 7.

As shown in Figure 2.7, a strong correlation exists between the second-order heterogeneous apparent rate constant and the activated carbons' textural properties; k_{Het} increases significantly both with mesopore surface area and micropore volume.

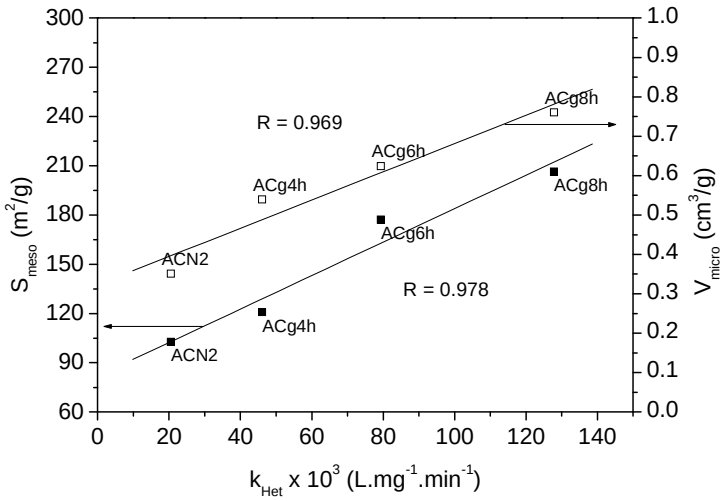

Figure 2.7 Variation of k_{Het} with selected activated carbons textural properties.

According to the previous reasoning, the decomposition of ozone in the presence of activated carbon is a surface phenomenon. Consequently, it directly relates with the textural properties of the activated carbon. The higher the available surface area for ozone adsorption, the faster is the decomposition.

2.3.2.3 Pre-ozonation of the activated carbon and cyclic experiments

The reutilisation of samples of AC_0 and $ACHNO_3$ was carried out with the purpose of studying the influence of the ozonation on the surface chemistry of the activated carbon, and the eventual deactivation during ozone decomposition.

In these experiments, a suspension of 0.5 g of the selected activated carbon (particle size = 0.6 - 1.18 mm) in 700 mL of phosphate pH 7 buffer solution saturated with ozone was tested on the decomposition of ozone. Due to the greater size of the activated carbon particles, the agitation provided was 500 rpm, in order to maintain the slurry perfectly mixed. After 30 min, the solution was filtered and the sample of

activated carbon was used in another run. This procedure was repeated four times for sample AC_0. In another series of experiments, both AC_0 and $ACHNO_3$ (particle size = 0.6 - 1.18 mm) were continuously ozonated in a phosphate buffer solution at pH 7 for 60 min. After this period, the samples were tested in the decomposition of ozone. The results obtained are shown in Figure 2.8 and Figure 2.9. The corresponding values of the heterogeneous apparent second-order rate constants are presented in Table 2.4.

Observing the curves and the respective k_{Het} values for ozone decomposition in the presence of AC_0, it is evident that there is a decrease in the activity of the activated carbon for decomposing ozone, particularly from the first to the second run. In the case of sample $ACHNO_3$, the small decrease from the first to the second run is within the experimental error.

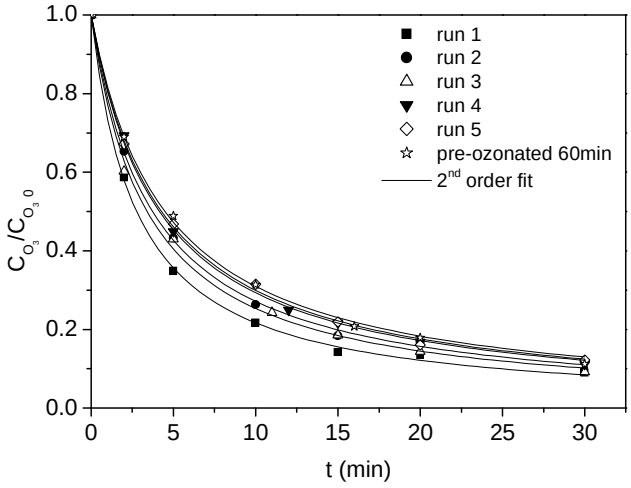

Figure 2.8 Influence of the pre-ozonation and reutilisation of AC_0 on the decomposition of ozone at pH 7.

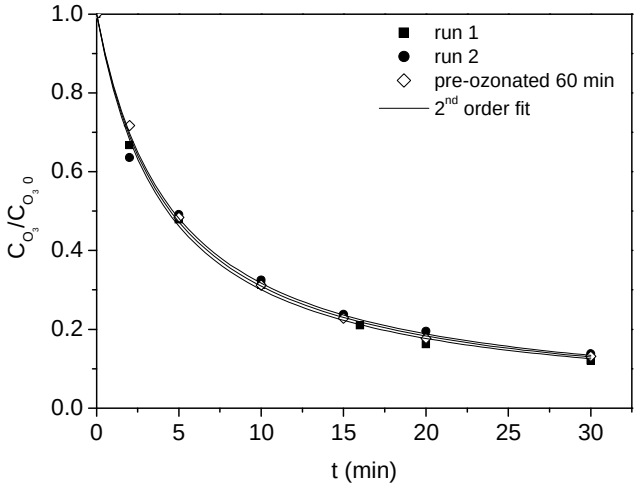

Figure 2.9 Influence of the pre-ozonation and reutilisation of $ACHNO_3$ on the decomposition of ozone at pH 7.

Table 2.4 k_{Het} values for cyclical utilisations (k_{Homog} = (11.9 ± 0.6) x 10^{-3} $L.mg^{-1}.min^{-1}$) and % O 1s obtained by XPS analysis.

	k_{Het} x 10^3 ($L.mg^{-1}.min^{-1}$)		% O 1s	
Run	AC_0	$ACHNO_3$	AC_0	$ACHNO_3$
0	-	-	5.6	10
1	24.7 ± 0.8	10.7 ± 0.6	-	-
2	12.5 ± 0.5	7 ± 1	-	19
3	15 ± 1	-	-	-
4	10.6 ± 0.5	-	-	-
5	9.4 ± 0.5	-	21	-
after pre-ozonation	9.2 ± 0.5	8.3 ± 0.4	23	22

After 60 min of exposure to a continuous flow of ozone, samples AC_0 and $ACHNO_3$ present a similar catalytic activity for the decomposition of dissolved ozone. This means that, despite their initial surface chemistry, after a certain exposure time to ozone in the liquid phase, they tend to behave in a similar way.

According to the results obtained by XPS analysis (Table 2.4), there is a significant increase in the amount of oxygen on the surface of the activated carbon samples after ozone treatment in the liquid phase and cyclical utilisations. It is interesting to note that, after a period of exposure to ozone, both AC_0 and $ACHNO_3$ samples have an equivalent amount of oxygen on their surface. In accordance with these results, it is possible to conclude that at least a fraction of the dissolved ozone is depleted in the oxidation of the activated carbon, particularly during the first cycles.

XPS is a surface technique which will provide an assessment of the chemical composition of the few uppermost layers of the material (2-5 nm) [24]. On the other hand, TPD profiles indicate the overall amount of surface oxygenated groups of the sample. The TPD spectra of samples AC_0 and $ACHNO_3$ before and after reaction at pH 7 are presented in Figure 2.10.

The increase in the amount of oxygenated groups in sample AC_0 confirms that this sample is, in fact, oxidised by dissolved ozone, but not to a great extent. The slight decrease in the activity of this sample in successive runs might be due to the introduction of some oxygenated electron-withdrawing groups that reduce the electron density of the activated carbon basal planes, thus disfavouring the adequate catalytic properties of the material for the decomposition of ozone, as discussed before. On the other hand, the TPD spectra of sample $ACHNO_3$ reveal that the amount of oxygen-containing surface groups before and after exposure to ozone is similar. Taking into account the results obtained by XPS, it is possible to conclude that dissolved ozone produces a mild oxidation of the activated carbon, mostly on the external surface. Nevertheless, this oxidation degree is not comparable to that produced by gaseous ozone [16, 28]. Hence, even after a few cycles of use, the activated carbon continues to be active in promoting ozone decomposition. Moreover, the textural properties of sample AC_0 remain constant after a period of 60 min of continuous exposure to ozone in the liquid phase (S_{BET} = 908 m^2/g, S_{meso} = 109 m^2/g and V_{micro} = 0.329 cm^3/g), as compared to the original sample (see Table 2.1).

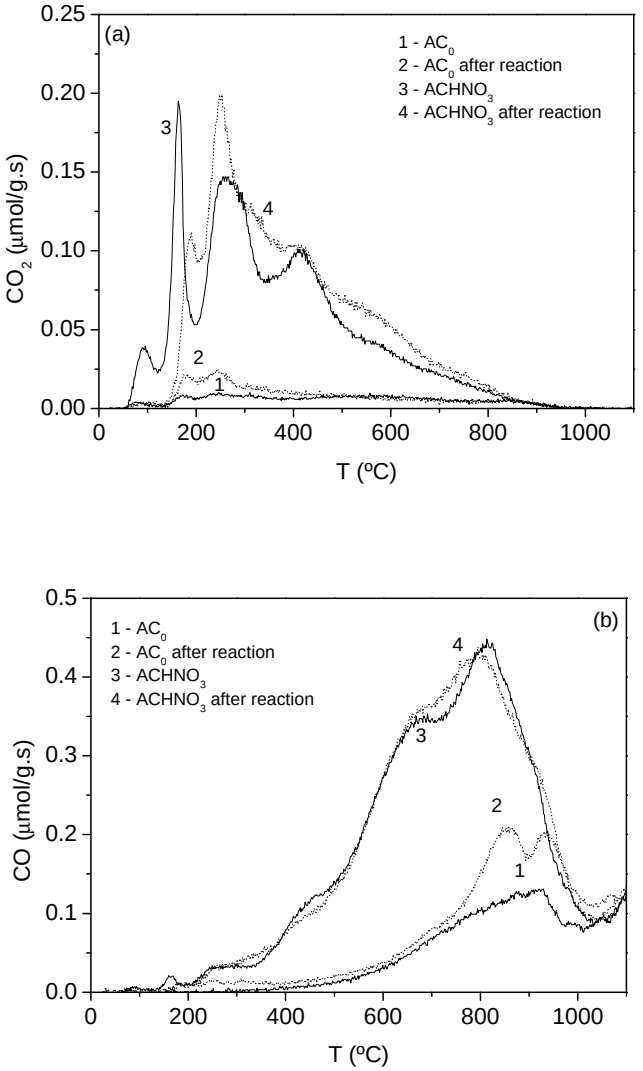

Figure 2.10 TPD spectra for samples AC_0 and $ACHNO_3$ before and after reaction at pH 7: (a) CO_2 evolution; (b) CO evolution (heating from room temperature to 1100 ºC at 5 ºC/min under 25 Ncm^3/min of He).

It is important to stress that the surface chemistry plays a role in the decomposition of ozone. However, because of the surface oxidation that occurs during this process, the influence of the surface chemistry tends to be attenuated along successive reutilisations of the catalyst. After a few cycles, basic activated carbons will behave

similarly to those with more acidic character due to the introduction of acid oxygenated groups on the surface.

2.4 Conclusions

The decomposition of ozone in the aqueous phase is controlled by the pH of the solution and is significantly enhanced in the presence of activated carbon.

Both textural and surface chemical properties of the activated carbon control the decomposition of ozone in water. In general, the process is favoured by activated carbons with large surface areas and high basicity. The influence of the activated carbon surface chemistry may be interpreted not only in terms of its electron donating capacity but also by taking into account dispersive and electrostatic interactions between the activated carbon surface and the solutes involved in the mechanism.

Successive experimental runs carried out with a fairly basic activated carbon sample show that the surface chemistry is only important in the first reaction cycles. It suffers a slight progressive oxidation by exposure to dissolved ozone, with a limited loss of activity, tending to behave as the acid activated carbons, which are still active catalysts.

The oxidation that leads to deactivation occurs mainly on the external surface of the carbon particles, keeping the textural properties practically unchanged.

The textural features of the activated carbon play a major role in the catalytic decomposition of ozone in the aqueous phase.

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Part III

Ozonation of Model Organic Compounds in the Presence of Activated Carbon

The main objective of this work is the development of catalytic ozonation systems for the application as tertiary treatments in the depuration of wastewater generated in the textile industry. Such liquid effluents vary greatly in their composition and chemical characteristics, even after biological treatment. Due to the complex matrix of real textile effluents, a deeper study into catalytic ozonation would not be possible to carry out with industrial effluents. Therefore, in order to understand the complex catalytic ozonation process, several organic pollutants were chosen as model compounds for the ozonation study.

Aniline and sulfanilic acid belong to the class of aromatic amines. Such compounds are generally refractory to biological treatments, and are amongst the by-products resultant from the anaerobic treatment of textile dyes. Additionally, benzenesulfonic acid was chosen for possessing a sulfonic group, which is commonly present in dye molecules from different classes. In this way it would also be possible to relate the reactivity of the different aromatic compounds with their substituent functional groups.

The ozonation of aromatic compounds may involve both direct and indirect pathways. The oxidation of such compounds leads to the formation of saturated aliphatic compounds such as aldehydes and carboxylic acids, which are generally more refractory to ozonation. Among the vast number of intermediates formed

during the oxidation of the selected compounds we focussed in following those that would persist, even for longer reaction periods. In this context, oxalic and oxamic acids were selected. The first one is the most common final oxidation product of a vast number of organic compounds. Moreover it is a quite simple molecule and, therefore, it was chosen as a model compound for more detailed mechanistic studies. The second one arises from the oxidation of nitrogen containing aromatic compounds, as is the case of aniline, sulfanilic acid and azo dyes, and is highly refractory to chemical oxidation. Very few information on this compound was found in the literature, as it is a less studied oxidation by-product. Due to their refractory character and simple molecular structure, these two particular carboxylic acids were also used as model compounds in order to clarify the mechanisms of ozonation in the presence of activated carbon at different solution pH.

The main goal in this part of the thesis is to study the catalytic ozonation of the selected compounds, in order to clarify the reaction mechanism and understand the influence of the activated carbon surface chemistry on the removal of those compounds, and on the mineralisation of the corresponding solutions. As pH values influence not only ozone decomposition in aqueous solution, but also surface properties of activated carbon and dissociation of organic molecules in water, different pH levels are also assessed.

This part is organised in four different chapters. The first one (chapter 3) is dedicated to the study of the adsorption of aniline, sulfanilic acid and benzenesulfonic acid on activated carbon. The surface chemical properties of activated carbon were found to influence the decomposition of ozone in the aqueous phase (see Part II), and it is well known that they play a role in the adsorption of organic compounds. Adsorption can also be an intermediated step in the catalytic ozonation process, and therefore this phenomenon should be studied. As no major differences were observed between the commercial activated carbon (AC_0) and the thermally treated sample (ACH_2), further work was carried out only with samples AC_0 and $ACHNO_3$. The following chapters refer to the activated carbon promoted ozonation of aniline (chapter 4), oxalic and oxamic acids (chapter 5), and finally, sulfanilic and benzenesulfonic acids (chapter 6). Some considerations on the possible reaction mechanisms involved are presented in the last two chapters.

3 Adsorption of Aromatic Compounds from the Biodegradation of Azo Dyes on Activated Carbon[1]

The adsorption of three selected aromatic compounds (aniline, sulfanilic acid and benzenesulfonic acid) on activated carbons with different surface chemical properties was investigated at different solution pH. A fairly basic commercial activated carbon was modified by means of chemical treatment with HNO_3, yielding an acid activated carbon. The textural properties of this sample were not significantly changed after the oxidation treatment. Equilibrium isotherms of the selected compounds on the mentioned samples were obtained and the results discussed in relation to their surface chemistry. The influence of electrostatic and dispersive interactions involved in the uptake of the compounds studied was evaluated. The Freundlich model was used to fit the experimental data. Higher uptakes are attained when the compounds are present in their molecular form. In general, adsorption was disfavoured by the introduction of oxygen-containing groups on the surface of the activated carbon.

3.1 Introduction

Aromatic amines such as aniline and sulfanilic acid appear in liquid effluents as a consequence of the biodegradation of several nitrogen containing organic compounds such as azo dyes [1, 2]. Among water treatment technologies, adsorption processes are largely employed and are advantageous from the point of view of micropollutant concentration.

Activated carbons present an outstanding adsorption capacity that stems from their high surface area, pore structure and surface chemical properties. These materials are effective adsorbents for priority pollutants, therefore being suitable for the

[1] Based on PCC Faria, JJM Órfão, JL Figueiredo, MFR Pereira, Appl Surf Sci 254 (2008) 3497–3503.

decontamination of water and wastewater. Currently, the use of activated carbon as a catalyst in advanced oxidation processes (AOPs), such as catalytic ozonation or wet air oxidation, for the removal of several organic compounds is being investigated [3-5]. Adsorption plays an important role in these processes. Therefore, the interactions of such compounds with the activated carbon surface must be studied in detail.

The adsorption capacity of an activated carbon is determined not only by its textural properties but also by the chemical nature of the surface, i.e. the amount and nature of surface functional groups [6]. It is also dependent on the properties of the adsorptive, such as molecular size, polarity, pKa and functional groups. Finally, solution pH, ionic strength and presence of other solutes also influence activated carbon adsorption performance. The nature of the surface functional groups can be modified through physical and chemical treatments, which include liquid phase oxidations with HNO_3 or H_2O_2 and gas phase oxidations with O_2 or N_2O, as well as thermal treatments at high temperatures in different gas environments (N_2, H_2) to selectively remove some of the functional groups [7]. For a broad range of pH, most of the aromatic pollutants are present in their molecular form. In this case π–π dispersive interactions are the predominant adsorption mechanism. In conditions where the solutes are dissociated, ions are present in solution and electrostatic interactions between them and charged surface functional groups play a role in adsorption [8]. A thorough knowledge of the activated carbon surface chemistry enables the preparation of adsorbents with appropriate characteristics for specific applications. The importance of this subject in the adsorption of several aromatic compounds has been recently reviewed [9, 10] and is highlighted in several papers [8, 11-15].

The removal of aniline, sulfanilic acid and benzenesulfonic acid from aqueous solutions by ozonation in the presence of activated carbons is studied in the scope of this thesis (chapters 4 and 6), as part of a more general research on the tertiary treatment of textile effluents by catalytic ozonation. Actually, at least some of those compounds (aniline, sulfanilic acid) may be produced during the biodegradation of textile azo dyes. On the other hand, it is imperative to consider the adsorption on activated carbon in order to discuss properly the associated kinetic results. As a matter of fact, adsorption competes with the oxidation reaction for pollutants removal and may be an important step in the catalytic ozonation mechanism. Although adsorption of aniline on activated carbon is rather well described in the

literature, data on sulfanilic and benzenesulfonic acid adsorption is quite scarce. Therefore, the present work intends to study the influence of the surface chemistry of activated carbon as well as the solution pH on the adsorption of the mentioned hazardous compounds, which are chemically different: aniline is an aromatic base, benzenesulfonic acid a strong aromatic acid and sulfanilic acid has both acid and basic groups. Three solution pH (3, 7 and 11) and two activated carbon samples with similar textural properties and different surface chemistry properties are considered in the present study.

3.2 Experimental

3.2.1 Preparation and characterization of activated carbon samples

A Norit GAC 1240 PLUS activated carbon was used as supplied as the starting material for this study (sample AC_0). This carbon was selected due to its good adsorption properties for water applications and a high purity level. It was submitted to an oxidation treatment in the liquid phase with HNO_3 6 M under boiling temperature during 3 h, yielding sample $ACHNO_3$ [11]. This treatment was carried out in order to obtain an activated carbon sample with acidic surface properties, while maintaining the original textural properties as far as possible.

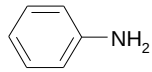
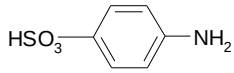
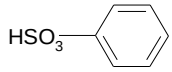
The textural characterization of the materials was based on the N_2 adsorption isotherms, determined at 77 K in a Coulter Omnisorp 100 CX apparatus. The micropore volumes (V_{micro}) and mesopore surface areas (S_{meso}) were calculated by the *t*-method using the standard isotherm proposed by Rodríguez-Reinoso et al. [16]. Two micropore structures were taken into account, and the corresponding volumes, W_{01} and W_{02}, were calculated [17]. The Stoeckli equation [18] was used to estimate the average micropore width of the smaller pores (L_1), using a value of 0.34 for the affinity coefficient of nitrogen.

The surface chemistry of the activated carbon samples was characterized by the determination of acidity and basicity, pH_{pzc}, and temperature-programmed desorption (TPD), as described elsewhere [11].

3.2.2 Adsorption experiments

Aniline, sulfanilic acid and benzenesulfonic acid were selected for the adsorption study. Some properties of these compounds are presented in Table 3.1.

Table 3.1 Properties of the selected aromatic compounds.

Solute		M (g/mol)	pKa	λ_{max} at pH 7 (nm)
Aniline		93.1	4.64*	280
Sulfanilic Acid (SA)		173.2	2.92*	248
Benzenesulfonic Acid (BSA)		158.2	-2.36	262

* pKa corresponding to the group NH_3^+

Adsorption isotherms were obtained at pH 3, 7 an 11 by mixing 50 cm^3 of solutions of different concentrations (10 – 500 mg/dm^3) with 50 mg of activated carbon (particle size = 100 - 300 μm) in closed Erlenmeyer flasks. The pH of the solutions was adjusted using NaOH or HCl solutions of different concentrations. The suspensions were shaken at room temperature for 24 h. From preliminary kinetic tests it was concluded that this time was enough to achieve equilibrium. Afterwards, the suspensions were centrifuged and the remaining concentration of the solute was determined in a JASCO V-560 UV-Vis spectrophotometer. For each solute the UV-Vis spectrum was determined and the maximum absorption wavelength identified (Table 3.1). This was done for all the pH values tested and the corresponding calibration curves were determined. The UV-Vis spectra of sulfanilic and benzenesulfonic acids did not change significantly with pH and λ_{max} was the same in the whole pH range studied (3 - 11). However, in the case of aniline, the λ_{max} shifted from 280 nm to 254 nm at pH = 3 due do the dominant presence of anilinium cations. As the absorptivity is quite low at this λ, for the adsorption isotherms determined at pH = 3, the activated carbon was removed, after reaching equilibrium, the pH of each remaining solution was raised to 7 and the absorbance measurements were done at 280 nm.

3.3 Results and discussion

3.3.1 Characterization of the activated carbon samples

The results obtained from the N_2 equilibrium adsorption isotherms at 77 K are presented in Table 3.2. As previously discussed [11, 19] no drastic changes in the textural properties of the prepared sample were observed, suggesting that the differences in the adsorption capacities of the samples will be mainly due to their chemical surface properties.

Table 3.2 Textural characterization of the AC samples.

Sample	S_{BET} (m^2/g)	S_{meso} (m^2/g)	V_{micro} (cm^3/g)	W_{01} (cm^3/g)	W_{02} (cm^3/g)	L_1 (nm)
AC_0	909	100	0.332	0.305	0.035	1.1
$ACHNO_3$	872	88	0.304	0.276	0.035	0.8

The results of pH_{pzc} and acidity-basicity are presented in Table 3.3. As expected, the basicity and pH_{pzc} decreased, while the acidity increased after the liquid phase oxidation of the activated carbon with HNO_3.

Table 3.3 Chemical characterization of the AC samples.

Sample	Acidity ($\mu mol\ g^{-1}$)	Basicity ($\mu mol\ g^{-1}$)	pH_{pzc}	CO [a] ($\mu mol\ g^{-1}$)	CO_2 [a] ($\mu mol\ g^{-1}$)
AC_0	211	352	8.5	579	63
$ACHNO_3$	1003	77	3.0	2122	559

[a] calculated by TPD spectra integration

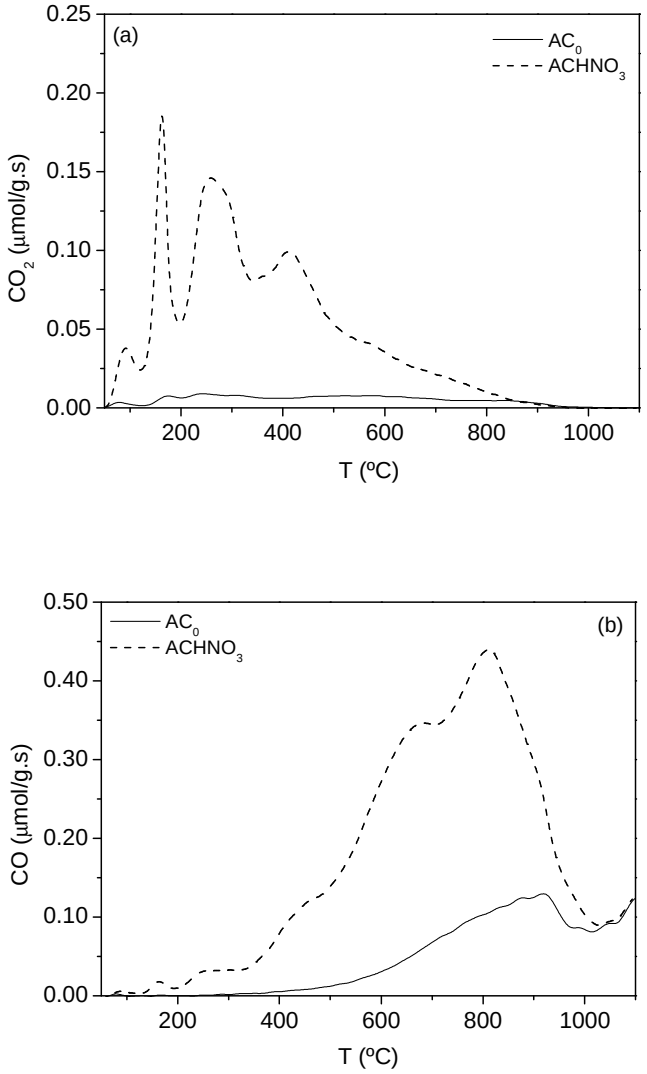


Figure 3.1 TPD spectra for samples AC_0 and $ACHNO_3$: (a) CO_2 evolution; (b) CO evolution (heating from room temperature to 1100 ºC at 5 ºC min^{-1} under 25 Ncm^3 min^{-1} of He).

Surface oxygenated groups on carbon materials decompose upon heating, releasing CO and/or CO_2 at different temperatures [7]. According to this, it is possible to identify and estimate the amounts of oxygenated groups on a given carbon. Comparing the TPD spectra presented in Figure 3.1 and the amounts of CO and

CO_2 released by samples AC_0 and $ACHNO_3$, obtained by integration of the TDP spectra (Table 3.3), it is clear that the treatment with HNO_3 originates a large amount of acidic oxygen containing groups on the surface of the activated carbon. The $ACHNO_3$ spectrum shows that this sample has a high amount of carboxylic acid groups (CO_2 evolved below 400 ºC) and anhydride groups (CO and CO_2 evolved around 550 ºC). Also some lactones are present (CO_2 evolved around 650 ºC). In addition there is a large amount of phenol and carbonyl groups (CO evolved around 700 ºC and 850 ºC, respectively). The latter functional groups are also present in sample AC_0, though in lower concentrations. Summarizing the results obtained from the different techniques, it is obvious that sample $ACHNO_3$ has a strong acid character while sample AC_0 is moderately basic.

3.3.2 Adsorption studies

Two parallel adsorption mechanisms, one involving electrostatic interactions and a second one involving dispersive interactions were reported to explain the adsorption of organic compounds on activated carbons [8]. Activated carbons are materials with amphoteric character; thus, depending on the pH of the solution, their surfaces might be positively or negatively charged. At $pH > pH_{pzc}$ the carbon surface becomes negatively charged favouring the adsorption of cationic species. On the other hand, adsorption of anionic species will be favoured at $pH < pH_{pzc}$ [20]. Basic carbons are characterized by a high content of electron rich sites on their basal planes and a low concentration of electron withdrawing groups [21]. The interaction between aromatic molecules and the activated carbon surface is expected to occur between the delocalised π electrons of the oxygen-free Lewis basic sites and the electrons of the aromatic ring. The same authors [21] have reported evidence for the protonation of basal plane sites on basic carbon. They state that oxygen-free carbon sites can adsorb protons from the solution, conferring a positively charged surface to the carbon. Thus, it is possible that negatively charged ions of the dissociated organic compounds also interact with these sites. On the other hand, the presence of oxygen-containing functional groups, which become negatively charged, has a negative effect on the adsorption of anionic species. In general, the presence of electron-withdrawing groups reduces the electron density on the surface of the carbon [8], thus decreasing its adsorption potential for the organic compounds.

The experimental results for the three compounds are presented and discussed separately in the following sections.

The classic equations of Langmuir (3.1) and Freundlich (3.2) were used to fit experimental isothermal equilibrium adsorption data:

$$q_e = q_m \frac{K_L C_e}{1 + K_L C_e} \quad (3.1)$$

$$q_e = K_F C_e^{1/n} \quad (3.2)$$

where C_e and q_e are the adsorptive equilibrium concentrations in the liquid and solid phases respectively, q_m is the maximum adsorption capacity according to the Langmuir model, K_L, K_F and n are constants. The equations parameters were calculated using non-linear fittings and are presented in Table 3.4, Table 3.5 and Table 3.6. Generally, it is the Freundlich model that better describes the adsorption data for the compounds studied. Therefore, only Freundlich fittings are represented along with experimental data in Figure 3.2, Figure 3.3 and Figure 3.4.

Table 3.4 Parameters of the Freundlich and Langmuir models for the adsorption isotherms of aniline on samples AC_0 and $ACHNO_3$ at different pH values.

Sample	pH	Freundlich model			Langmuir model		
		K_F $((mmol/g_{AC})(L/mg)^{1/n})$	n	R^2	qm $(mmol/g_{AC})$	K_L (L/mmol)	R^2
AC_0	3	0.32 ± 0.02	8 ± 4	0.496	0.38 ± 0.02	9 ± 4	0.693
	7	1.48 ± 0.02	4 ± 2	0.993	1.9 ± 0.1	7 ± 3	0.907
	11	1.52 ± 0.02	4.0 ±0.2	0.992	1.9 ± 0.1	6 ± 2	0.916
$ACHNO_3$	3	0.31 ± 0.02	7 ± 2	0.621	0.38 ± 0.02	7 ± 2	0.804
	11	0.83 ± 0.02	4.1 ± 0.3	0.992	1.09 ± 0.05	6 ± 2	0.932

Table 3.5 Parameters of the Freundlich and Langmuir models for the adsorption isotherms of sulfanilic acid on samples AC_0 and $ACHNO_3$ at different pH values.

Sample	pH	Freundlich model			Langmuir model		
		K_F $((mmol/g_{AC})(L/mg)^{1/n})$	n	R^2	qm $(mmol/g_{AC})$	K_L (L/mmol)	R^2
AC_0	3	0.58 ± 0.02	6.9 ± 0.9	0.957	0.6 ± 0.1	(2 ± 2)x10	0.617
	7	0.30 ± 0.01	7 ± 1	0.914	0.28 ± 0.02	(1.1 ± 0.7)x10^3	0.788
	11	0.253 ± 0.003	4.1 ± 0.2	0.993	0.28 ± 0.02	12 ± 5	0.865
$ACHNO_3$	3	0.339 ± 0.008	3.6 ± 0.3	0.979	0.38 ± 0.04	9 ± 5	0.830
	11	0.094 ± 0.002	1.40 ± 0.05	0.996	0.39 ± 0.08	0.3 ± 0.1	0.984

Table 3.6 Parameters of the Freundlich and Langmuir models for the adsorption isotherms of benzenesulfonic acid on samples AC_0 and $ACHNO_3$ at different pH values.

Sample	pH	Freundlich model			Langmuir model		
		K_F $((mmol/g_{AC})(L/mg)^{1/n})$	n	R^2	qm $(mmol/g_{AC})$	K_L (L/mmol)	R^2
AC_0	3	0.49 ± 0.02	13 ± 7	0.550	0.52 ± 0.03	(2 ± 2)x10	0.457
	7	0.30 ± 0.01	6 ± 1	0.867	0.31 ± 0.02	(4 ± 2)x10	0.565
	11	0.218 ± 0.005	7.0 ± 0.9	0.916	0.23 ± 0.01	24 ± 9	0.729
$ACHNO_3$	3	0.34 ± 0.01	5.2 ± 0.8	0.904	0.35 ± 0.03	(4 ± 4)x10	0.489
	11	0.076 ± 0.005	2.3 ± 0.5	0.858	0.13 ± 0.03	1.5 ± 0.9	0.740

Since there were no drastic changes in the textural properties of the activated carbon, the disparity in the uptakes for the different activated carbons may be explained almost entirely by the differences in the chemical nature of the samples.

3.3.2.1 Aniline

The aniline adsorption isotherms at room temperature determined at different pH values are presented in Figure 3.2 and the respective Freundlich and Langmuir parameters are listed in Table 3.4.

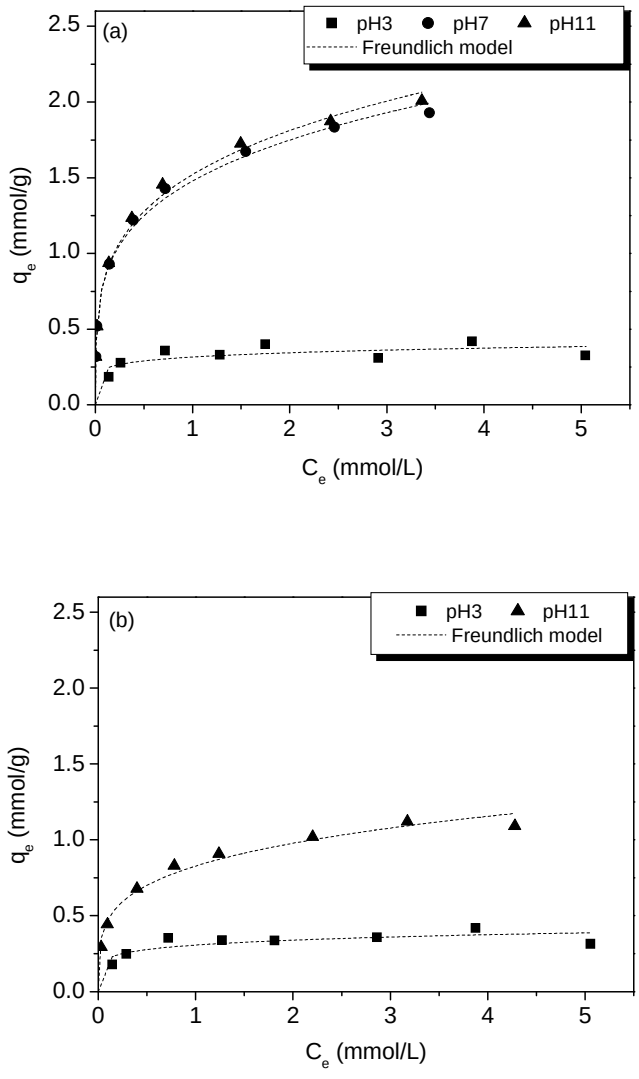


Figure 3.2 Adsorption isotherms of aniline at room temperature on samples (a) AC_0 and (b) $ACHNO_3$ at different solution pH.

The aniline uptake is significantly lower at pH 3 than at pH 7 and 11. At pH 7 and pH 11, aniline in aqueous solution is mainly in its molecular form. In this case adsorption is believed to occur mainly through dispersive interactions between the aromatic ring and the π electrons of the graphitic structure of the activated carbon. At pH 11 the highest uptake was observed for sample AC_0 as a result of a higher electronic density on its basal planes. Due to the presence of oxygen-containing surface groups, which are electron withdrawing groups, dispersive interactions between aniline molecules and sample $ACHNO_3$ are disfavoured. Therefore, the adsorption capacity of this sample is lower.

At pH 3 the surface of AC_0 is positively charged ($pH < pH_{pzc}$), while sample $ACHNO_3$ presents a neutral surface ($pH = pH_{pzc}$). Electrostatic repulsions are expected to occur between AC_0 and anilinium cations, which predominate in solution at this pH. However, both samples AC_0 and $ACHNO_3$ adsorb similar amounts of solute. It may be concluded that electrostatic repulsions did not play an important role in this case. This observation leads to the conclusion that, even though adsorption of cationic species on activated carbons is enhanced by the presence of surface acid groups, basic carbons still present a relatively good performance, indicating that dispersive interactions between the delocalised π electrons on the surface of the basic activated carbons and the free electrons of the anilinium aromatic ring play a dominant role in the adsorption mechanism. The results obtained are in agreement with those of Villacañas et al. [15] when studying the adsorption of several aromatic compounds in another commercial activated carbon.

3.3.2.2 Sulfanilic Acid

Sulfanilic acid is more adsorbed on activated carbon at acid pH than at neutral and basic pH (Table 3.5 and Figure 3.3). When the pH is raised above pKa, both substituting groups are deprotonated and the compound is mainly in its anionic form (NH_2-Ar-SO_3^-). When the solution pH is raised above the pH_{pzc} of the carbon, the surface of the activated carbon becomes negatively charged, thus disfavouring the adsorption of anionic species. Comparing sulfanilic acid adsorption uptake at different pH values, it is obvious that adsorption on samples AC_0 and $ACHNO_3$ is favoured at low pH, as can be observed in Figure 3.3.

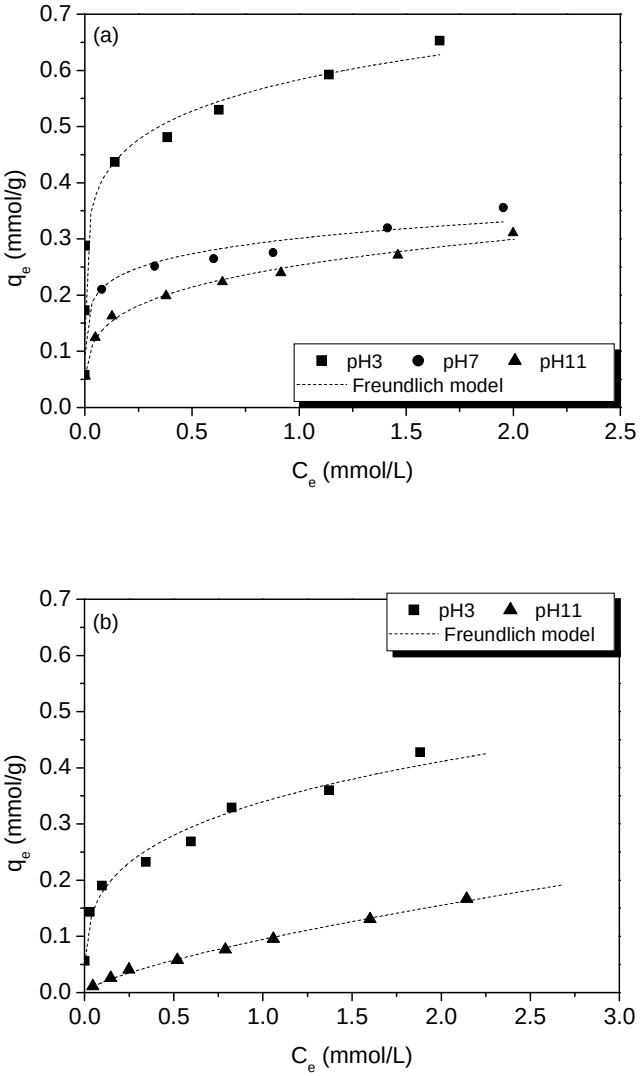


Figure 3.3 Adsorption isotherms of sulfanilic acid at room temperature on samples (a) AC_0 and (b) $ACHNO_3$ at different solution pH.

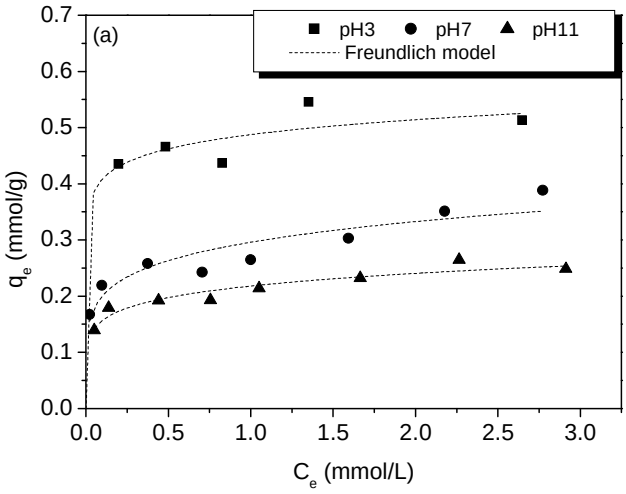
Both at pH 3 and 11, sample AC_0 adsorbs higher amount of sulfanilic acid than sample $ACHNO_3$. As the materials have similar textural properties, the differences may be explained in terms of their surface chemical properties. Sample AC_0 has a higher electronic density due to the low content of surface oxygen-containing groups, and therefore adsorption is favoured. At pH 11, both samples are negatively

charged, but repulsive interaction between sulfanilic acid conjugated anions and activated carbon negatively charged surface groups are stronger in sample $ACHNO_3$ than in sample AC_0.

3.3.2.3 Benzenesulfonic acid

The adsorption isotherms obtained for this compound at different pH values are present in Figure 3.4. Table 3.6 shows the corresponding Freundlich and Langmuir parameters.

Benzenesulfonic acid is a strong acid (pKa = -2.36); thus it is in the corresponding deprotonated form (anionic) in the whole range of studied pH. According to the results obtained, benzenesulfonic acid uptake by both activated carbon samples decreases with an increase in pH and this is explained on the basis of the nature of its interaction with activated carbon surface. The surface of sample AC_0 tends to become negatively charged as the pH increases to 11 ($pH > pH_{pzc}$), increasing the electrostatic repulsions between AC surface groups and the conjugated anions of benzenesulfonic acid. When comparing adsorption uptakes obtained in the two activated carbon samples, it is observed that $ACHNO_3$ adsorbs lower amounts of benzenesulfonic acid than sample AC_0, due to the existence of stronger electrostatic repulsive interactions and a lower electronic density on the corresponding surface.



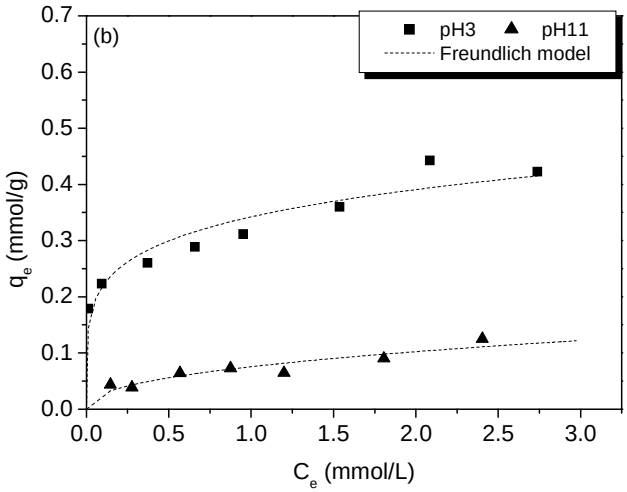


Figure 3.4 Adsorption isotherms of benzenesulfonic acid at room temperature on samples (a) AC_0 and (b) $ACHNO_3$ at different solution pH.

3.4 Conclusions

The adsorption of aniline, sulfanilic acid and benzenesulfonic acid on activated carbon is governed by the pH of the solution, by the pKa of the substances and by the chemical properties of activated carbon.

The adsorption phenomenon is ruled by two different types of interactions: dispersive interactions between delocalized π electrons of the activated carbon basal planes and the electrons of the aromatic ring of the selected organic compounds, and electrostatic interactions between charged oxygenated groups on the AC surface and ionic species resultant from the dissociation of the solutes in aqueous solution.

For molecules with basic properties, such as aniline, adsorption is favoured at neutral and basic pH. For compounds with acidic character, adsorption will be favoured at low solution pH.

Regardless of the nature of the adsorptive molecule, higher adsorption uptakes were achieved with sample AC_0, which confirms that the existence of electron

withdrawing groups on the surface of the AC is detrimental for adsorption of aromatic compounds.

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4 Ozonation of Aniline Promoted by Activated Carbon[1,2]

The removal of aniline from aqueous solutions by ozonation promoted by activated carbon was investigated at different solution pH. For comparative purposes, single ozonation and adsorption on activated carbon were carried out in the same experimental set-up. In order to evaluate the role of the activated carbon surface chemistry during ozonation, a commercial activated carbon, Norit GAC 1240 PLUS, was submitted to oxidation in the liquid phase with HNO_3. The texture and surface chemistry of the activated carbon samples were characterised. During ozonation, complete conversion of aniline was achieved after approximately 20 min, regardless of the presence of activated carbon. The partial oxidation of aniline originates several by-products. Nitrobenzene, *o*-aminophenol and *p*-aminophenol were the primary aromatic oxidation by-products identified during the ozonation reactions. In terms of mineralisation, best results were achieved by the simultaneous use of ozone and activated carbon. Though there is a strong contribution of adsorption, a considerable synergetic effect between ozone and activated carbon is observed. In general, activated carbon promotes the reaction of ozonation enhancing the efficiency of this treatment process. The basic activated carbon presented greater activity in this process, leading to higher mineralisation rates.

4.1 Introduction

Aniline and its derivatives are widely used in the chemical industry, mainly in the synthesis of rubber additives and polymers, and in the production of pharmaceuticals, agricultural chemicals and pesticides. Additionally, aniline is an important intermediate in the production of dyes and pigments. Consequently, such

[1] Based on PCC Faria, JJM Órfão, MFR Pereira, Chemosphere 67 (2007) 809–815.

[2] Additional data presented in Appendix C.

compounds are frequently found in industrial wastewater. Aniline is refractory to biodegradation and is one of the aromatic amines resultant from the anaerobic biodegradation of some aromatic compounds, such as azo dyes [1]. It is a toxic substance to the human and to the aquatic life, and it is easily adsorbed in sediments, fact that can extend its persistence in the aquatic environment [2]. Due to the negative environmental impact caused by the high toxicity of aniline, wastewater containing such compound demand thorough treatment before being discharged in natural water courses. Due to its refractory character towards oxidation, the treatment of aniline, even at low concentrations, requires the use of strong oxidising agents such as ozone.

Ozonation processes are widely used in the fields of water and wastewater treatments [3, 4]. In general, ozone does not completely oxidise organic compounds to CO_2 and H_2O, due to the formation of partial oxidation products relatively unreactive towards ozone; therefore, several approaches have been taken to improve the oxidising power of this technique. In order to enhance the efficiency of ozone based oxidation processes, the combination of ozone with UV radiation, H_2O_2, metallic ions or heterogeneous catalysts, with or without metallic phases, has been investigated [3]. Overall, these processes aim at the transformation of ozone into highly reactive oxidant species, such as hydroxyl radicals ($HO^{\bullet}$), which have a high reactivity towards a vast range of organic pollutants and are less selective than molecular ozone. Consequently, they play an important role in the mineralisation of refractory organic compounds [5, 6], leading to an enhanced removal of total organic carbon (TOC).

The combination of ozone and activated carbon in a single step was found to be an attractive alternative to the treatment of wastewater containing dyes or other organic contaminants [7-11]. The mentioned works report significant synergetic effects and enhanced mineralisation degrees in the degradation of numerous organic compounds by the simultaneous use of ozone and activated carbons. Therefore, processes combining these two agents appear to be promising in the treatment of a number of aromatic compounds and subsequent oxidation by-products. Activated carbon was found to accelerate the decomposition of ozone into highly oxidative species such as hydroxyl radicals [12], which have a critical role in the mineralisation of organic compounds. According to recent publications [13, 14], the decomposition of dissolved ozone in the presence of activated carbon is dependent on both chemical and textural features of this material.

Despite the investigation recently carried out on ozonation of several organic pollutants in the presence of activated carbon, there are doubts about the reaction mechanism. Among the possible mechanisms suggested in the literature, the following approaches seem to be feasible possibilities: activated carbon promotes the decomposition of O_3 into $HO^{\bullet}$ or other highly active oxygenated radicals and the oxidation occurs in the homogeneous phase; or activated carbon adsorbs the organic compounds, which then react on the surface, either with O_3 or oxygenated radicals. It is probable that both mechanisms occur simultaneously. Generalization concerning the mechanisms of catalytic ozonation is difficult as it depends, among other factors, on the nature of the catalyst and the organic compound to be oxidized [3].

Concerning the ozonation of aniline, which is an aromatic compound with an unshared electron pair, the direct electrophilic attack by ozone is favoured. In this case, the by-products obtained are mainly aldehydes, ketones, acids and nitro compounds. Aniline can also be attacked by hydroxyl radicals originated from ozone self-decomposition, leading to the formation of azo-derivatives and hydroxylated compounds. Both mechanisms are favoured at basic pH where the electrophilic character of the molecule is enhanced [15]. As a result of aniline oxidation, several classes of organic by-products have been identified. One of them consists of nitrogenated compounds such as nitrosobenzene, nitrobenzene, aminophenol, etc. Another group is composed by condensation products such as azobenzene and azoxybenzene resulting from the reaction between aniline molecules and products from its partial oxidation, which are usually coloured. The rupture of the N-C bond leads to the formation of hydroquinone, benzoquinone [15], and the cleavage of the aromatic ring leads to the formation of significant amounts of saturated organic compounds such as aldehydes, ketones and mostly carboxylic acids. The latter are highly resistant to ozone attack and tend to accumulate in water. Nevertheless, the removal of such compounds can be achieved by advanced oxidation treatments such as catalytic ozonation.

In this work, two activated carbon samples differing mainly in their surface chemical properties, AC_0 and $ACHNO_3$, were used to investigate the catalytic ozonation of aniline. The influence of solution pH on adsorption, ozonation and ozonation promoted by activated carbon was considered. The kinetics of aniline removal and the formation and disappearance of aromatic oxidation by-products

were followed by HPLC. Also, the mineralisation degree was followed by TOC analysis.

4.2 Experimental

4.2.1 Ozonation experiments

The removal of aniline from aqueous solutions at different pH values was investigated in a slurry lab-scale reactor (ca. 1 L) equipped with agitation and recirculation jacket (see Appendix A). For comparative purposes, both adsorption on activated carbon and ozonation experiments in the absence of activated carbon were performed in the same system, under identical experimental conditions. Two activated carbons with different surface chemistries were assessed. Sequential experiments of ozonation followed by adsorption on activated carbon were also carried out, with the purpose of evaluating the catalytic and adsorption contributions of the activated carbon to the process. In each experiment the reactor was filled with 700 mL of buffered solution of aniline 1.1 mM at the desired pH. In the adsorption and catalytic experiments, 350 mg of activated carbon (particle size = 100 - 300 μm) were introduced in the reactor. Ozone was produced from pure oxygen in a BMT 802X ozone generator. The experiments were performed at constant gas flow (150 cm^3 min^{-1}, measured at room T and P) and constant inlet ozone concentration (50 g Nm^{-3}). The concentration of the ozone in the gaseous phase was monitored with a BMT 964 ozone analyzer. Ozone in the gas phase leaving the reactor was removed in a series of gas washing bottles filled with iodide potassium (KI) solution. The agitation was maintained constant at 300 rpm in order to keep the reactor content perfectly mixed. The temperature was controlled by a thermostatic bath. All the experiments were performed at 25 ºC and different solution pH (3, 7, 9).

Aniline and the oxidation products formed during reaction were analysed with a Hitachi Elite Lachrom HPLC equipped with a diode array detector. The stationary phase was a Purospher Star RP-18 5μm column (250 mm x 4.6 mm) working at room temperature with an eluent solution of acetonitrile and water, under gradient mode. The degree of mineralisation was followed by TOC analysis in a Shimadzu TOC-5000A Analyzer.

4.2.2 Preparation and characterization of activated carbons

A commercial activated carbon, Norit GAC 1240 PLUS (sample AC_0), was submitted to an oxidation treatment in the liquid phase with HNO_3 6 M under boiling temperature during 3 h (sample $ACHNO_3$). The textural characterization of the materials was based on the N_2 adsorption isotherms determined at 77 K. The surface chemistry of the activated carbon samples was characterised by the determination of acidity and basicity, pH_{pzc}, and temperature-programmed desorption (TPD), as described elsewhere [16].

4.3 Results and Discussion

4.3.1 Characterization of activated carbons

The physical and surface chemical properties of the activated carbon samples used in this study are summarized in Table 4.1.

Table 4.1 Characterization of activated carbon samples.

Sample	S_{BET} ($m^2\ g^{-1}$)	S_{meso} ($m^2\ g^{-1}$)	V_{micro} ($cm^3\ g^{-1}$)
AC_0	909	100	0.332
$ACHNO_3$	827	88	0.304

Sample	Acidity ($\mu mol\ g^{-1}$)	Basicity ($\mu mol\ g^{-1}$)	pH_{pzc}	CO [a] ($\mu mol\ g^{-1}$)	CO_2 [a] ($\mu mol\ g^{-1}$)
AC_0	211	352	8.5	579	63
$ACHNO_3$	1003	77	3.0	2122	559

[a] calculated by TPD spectra integration

Analysis of the characterization results obtained for samples AC_0 and $ACHNO_3$ shows that no major differences in the textural properties of these materials were observed. As expected, the surface acidity increased for sample $ACHNO_3$ due to the introduction of several oxygen-containing functional groups, namely carboxylic acids, whereas the surface basicity decreased. Accordingly, the HNO_3 treatment yields samples with low pH_{pzc}. Comparatively, sample AC_0 has a moderate basic

character and higher pH_{pzc}. According to the TPD results (Table 4.1), sample $ACHNO_3$ releases higher amounts of CO and CO_2 which indicates a greater content of surface oxygen-containing groups than sample AC_0. It is known that both textural and surface chemical properties control the decomposition of ozone in water [13, 14] (see chapter 2). In this work, the performances of the two mentioned activated carbon samples, differing mainly in their chemical surface properties, are compared in the ozonation of aniline.

4.3.2 Ozonation of aniline

4.3.2.1 Influence of chemical characteristics of activated carbon and solution pH

In order to test the influence of the activated carbon properties on the removal of aniline from the aqueous phase, single ozonation and ozonation in the presence of two samples of activated carbon (AC_0 and $ACHNO_3$) were carried out. For comparative purposes adsorption of aniline on both activated carbons was also studied. Figure 4.1 shows the evolution of dimensionless aniline concentration, and TOC removal with time, at pH 3, 7 and 9. Both for ozonation in the presence or absence of activated carbon, the curves corresponding to aniline decay were well fitted by a first order kinetic model. The respective apparent first order rate constants obtained at pH 3, 7 and 9 are presented in Table 4.2.

In all cases, whenever ozone was used, a fast decay of aniline concentration was observed and complete removal was achieved after approximately 20 min of reaction. Ozonation is an efficient process for the degradation of compounds containing either an activated aromatic ring or double bonds, as ozone selectively attacks these structures. The amino group ($-NH_2$) is electron donating and thus, it activates the aromatic ring by increasing its electronic density. Aromatic compounds having a higher delocalisation of electrons exhibit higher reactivity towards ozone. Therefore, these compounds are likely to suffer electrophilic attack by ozone.

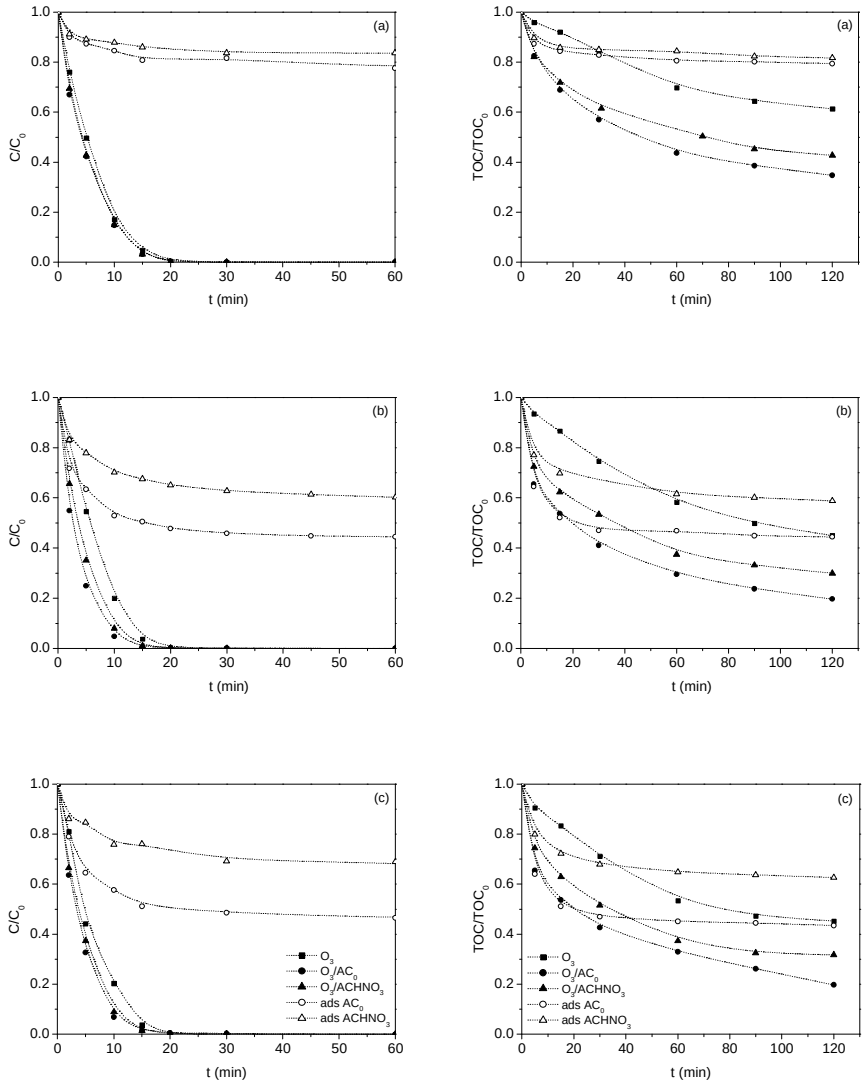

Figure 4.1 Evolution of dimensionless aniline concentration and TOC during ozonation, ozonation in the presence of activated carbons AC_0 and $ACHNO_3$, and adsorption on both activated carbons at (a) pH 3, (b) pH 7 and (c) pH 9.

In water, only part of the dissolved ozone reacts directly with the dissolved solutes. Another part is catalytically decomposed by hydroxide ions and other solutes [5], leading to the formation of $HO^{\bullet}$ radicals. Due to the role of the hydroxide ion in initiating the decomposition of ozone in water, the contribution of indirect

ozonation reactions is especially important at basic pH. Hydroxyl radicals are highly reactive and are responsible for the mineralisation of a vast range of organic compounds. Consequently, a faster disappearance of aniline would be expected at pH 7 and 9. Moreover, at pH 3 the amino group of aniline remains predominantly in its protonated form, AR-NH_3^+ (pKa = 4.87), which is an electron withdrawing group. It would be expected that the electrophilic attack by molecular ozone would be slower in this case than at neutral and basic pH. However, under the experimental conditions used in this work no direct relation between pH and aniline decay was observed for single ozonation, which is confirmed by the apparent first order rate constants values presented in Table 4.2. On the other hand, when comparing TOC removal by single ozonation at different pH values, especially for longer reaction periods, it is evident that a pH effect exists. According to the results depicted in Figure 4.1, the amount of organic carbon removed was higher at pH 7 and 9 than at pH 3, which means that the mineralisation of reaction intermediates is enhanced by the presence of higher concentrations of $HO^{\bullet}$ species.

Table 4.2 First order apparent rate constants of aniline removal by ozonation and ozonation in the presence of different activated carbon.

pH	O_3			O_3/AC_0			$O_3/ACHNO_3$		
	k (min^{-1})		R^2	k (min^{-1})		R^2	k (min^{-1})		R^2
3	0.16	± 0.01	0.992	0.188	± 0.007	0.997	0.184	± 0.007	0.997
7	0.15	± 0.01	0.980	0.290	± 0.005	0.999	0.221	± 0.008	0.998
9	0.16	± 0.01	0.992	0.233	± 0.007	0.997	0.211	± 0.008	0.997

The simultaneous use of ozone and activated carbon improves the rate of aniline removal, especially at pH 7 and 9 (see Table 4.2), which might be explained by a sum of contributions of direct and indirect ozonation, and adsorption on activated carbon. Comparing the two activated carbon samples, this effect is slightly more pronounced for sample AC_0.

The adsorption of aniline is highly influenced by the solution pH and by the surface chemistry of the activated carbon [17] (see chapter 3). According to the characterization of the activated carbons used in this work, sample AC_0 is considered a basic activated carbon. Basic activate carbons are characterised by having free π electrons on their basal planes. Its surface is almost free from oxygen-

containing groups and it has a high pH_{pzc}. On the other hand $ACHNO_3$ is an acid activated carbon due to the presence of oxygen containing surface groups, namely carboxylic groups, which are electron-withdrawing groups. At pH 7 and 9 aniline is present in solution in its molecular form. It adsorbs on the activated carbon through dispersive interactions between the free electrons of the activated carbon surface and the electrons of the aromatic ring. Since AC_0 has a higher electron density, it adsorbs more aniline than sample $ACHNO_3$. When comparing adsorption at different solution pH, it is obvious that higher amounts of aniline are adsorbed at pH 7 and 9 than at pH 3. At acid pH < pKa, aniline predominates in solution in its protonated form (cation anilinium), which is less adsorbed than the corresponding molecular form. Moreover, at this pH, AC_0 is positively charged, therefore there are repulsive electrostatic interactions between the activated carbon and aniline species. The differences observed between both activated carbon samples are due to their distinct surface chemical properties.

Considering only the removal of aniline, there is no great advantage in adding activated carbon to the process, once it is possible to efficiently remove aniline by single ozonation, as previously shown. However, when observing the TOC removal along time, the advantage of using ozone and activated carbon becomes obvious (see Table 4.3).

Table 4.3 TOC removal achieved after ozonation of aniline in the absence or in the presence of activated carbon.

pH	% TOC removal					
	O_3		O_3/AC_0		$O_3/ACHNO_3$	
	30 min	120 min	30 min	120 min	30 min	120 min
3	15.5	38.6	42.9	65.2	38.5	57.3
7	25.4	55.0	58.9	80.3	46.6	70.1
9	28.9	54.7	57.4	80.3	48.5	68.3

Regardless of the solution pH, the addition of a small amount of activated carbon (0.5 g L^{-1}) during the ozonation of aniline increases considerably the percentage of TOC removal. After 120 min of reaction, the increase in TOC removal relatively to single ozonation was of ca. 27% at pH 3 and 25% at pH 7, when using sample AC_0.

At both pH conditions the use of sample $ACHNO_3$ instead of sample AC_0 resulted in slight inferior TOC removal. This difference is attributed to the different surface chemical properties of the activated carbons, which influence both their adsorption capacities and the ability to catalyse the decomposition of ozone [13]. During the experiments at basic pH, CO_2 tend to accumulate in aqueous solution in the form of HCO_3^- and CO_3^{2-} (inorganic carbon), which are know to be $HO^{\bullet}$ scavengers. Thus, despite the higher ozone decomposition rate at pH 9 reported before [13] (see chapter 2), the overall TOC removal results obtained at pH 9 are quite similar to those obtained at pH 7.

It is important to stress that, while aniline is removed, oxidation by-products are formed and stay in solution for further mineralisation. In this work, only aromatic by-products were detected but, according to the literature, final ozonation products are mainly saturated aliphatic compounds. Such oxidation products are relatively unreactive towards ozone, but are likely to be attacked by $HO^{\bullet}$ radicals [18]. As activated carbon is believed to promote the decomposition of ozone yielding $HO^{\bullet}$ radicals in solution [12], the role of activated carbon in the ozonation of organic compounds becomes crucial in the mineralisation of refractory oxidation by-products. The analytical methods used in this work did not enable the identification of aliphatic oxidation by-products. Thus, mineralisation of such compounds was followed just by TOC analysis.

4.3.2.2 Aniline ozonation by-products

As a result of the degradation process of aniline in the presence of ozone several intermediates are formed. It was observed that, during the first minutes of reaction, the solution changed from uncoloured to a brown-yellowish colour. This was due to the formation of by-products via N-N condensation which are often coloured due to the presence of azo bond ($-N=N-$), a well known chromophore group [15]. After a few minutes of ozonation the solution became colourless again. This means that those coloured compounds formed in the beginning of the reaction were also oxidized to other colourless compounds.

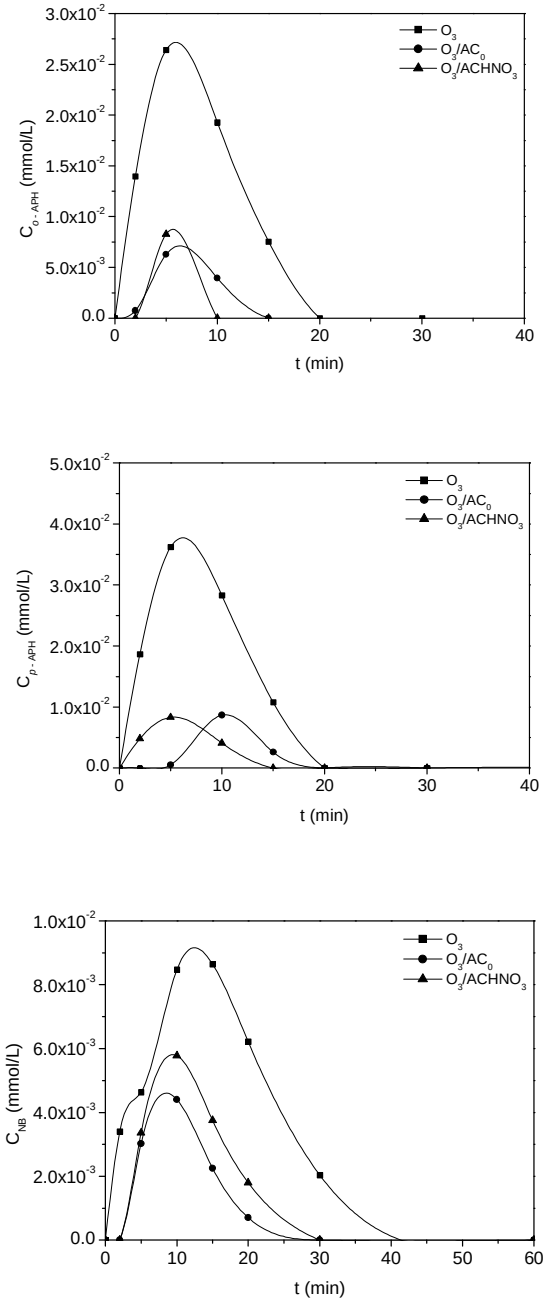

Figure 4.2 Evolution of concentrations of o-aminophenol (*o*-APH), *p*-aminophenol (*p*-APH), and nitrobenzene (NB) during ozonation (■) and ozonation in the presence of AC_0 (●) and $ACHNO_3$ (▲) at pH 7.

Nitrobenzene, *o*-aminophenol and *p*-aminophenol were the primary aromatic oxidation by-products detected and quantified. Other unidentified organic products were also detected in the chromatograms. The formation and disappearance of the mentioned by-products followed similar trends in the presence or absence of activated carbon. However, in the presence of activated carbon, the concentration of the detected compounds was always lower, comparatively to single ozonation, which can be explained by a faster oxidation via $HO^{\bullet}$ and/or adsorption and/or reaction on the activated carbon surface. The results obtained at pH 7 are presented in Figure 4.2. Similar trends were observed at the other two pH levels studied (see Appendix C).

The disappearance of nitrobenzene is slower than that of *o*- and *p*-aminophenol which might be due to the nature of benzene substituents. Electron donating groups increase the reactivity of the ring, whereas electron withdrawing groups lead to a decrease in the ozonation rate constants [4]. While $-NH_2$ and -OH are activating substituents, thus increasing the electronegativity of the aromatic ring, $-NO_2$ is an electron withdrawing group. Therefore nitrobenzene is less reactive than aminophenol. It is important to emphasize that in all the ozonation experiments, the chromatograms obtained after ca. 30 min of reaction revealed the total absence of aromatic compounds, except for nitrobenzene in the case of single ozonation. As stated before, ozone reacts quite efficiently with these compounds, fact that justifies their fast elimination from solution. Nevertheless, at this point of the reaction, the amount of organic carbon in solution is still high (see Table 4.3). Observing the concentrations of these compounds along time, it is obvious that they represent only a very small fraction of the total amount of aniline oxidation by-products. Although these have not been identified, it is known that, depending on the experimental conditions, these compounds are oxidised to other intermediates and finally to saturated small chain carboxylic acids [18], being oxalic acid one of the most relevant oxidation by-products. Preliminary results have shown that when the reaction is not carried out in a buffered solution, the pH decreases significantly (ca. 3), indicating the formation of acid compounds. Carboxylic acids are low reactivity compounds towards ozone but may be oxidized by secondary oxidants, such as $HO^{\bullet}$ radicals, produced by a preliminary decomposition of aqueous ozone. Even though they are oxidized by $HO^{\bullet}$ radicals, their oxidation rate is usually lower than their formation rate. Therefore they accumulate during ozonation processes [4]. Thus, extended reaction time is needed for complete mineralisation of such compounds.

According to the results presented in this work, the ozonation of aniline in the presence of activated carbon results in a high level of TOC removal comparatively to single ozonation. Such observation suggests that activated carbon contributes to the mineralisation of refractory oxidation by-products, probably because of an enhanced transformation of ozone into highly reactive species, such as $HO^{\bullet}$ radicals.

4.3.2.3 The role of the activated carbon during ozonation of aniline

Sequential experiments of ozonation followed by adsorption on both activated carbons were carried out as follows, with the purpose of evaluating the type of contribution of the activated carbon to the process. A solution of aniline (C_0 = 1.1 mM) was ozonised for 30 min. Then, oxygen was bubbled in the solution in order to eliminate the dissolved ozone. Subsequently, 350 mg of activated carbon were introduced in the reactor. The period of adsorption last for 30 min. Samples from the solution were withdraw, after the periods of ozonation and adsorption, for TOC analysis. The results obtained are shown in Figure 4.3, and compared to those obtained by ozonation and ozonation in the presence of each activated carbon sample, after 30 min of reaction.

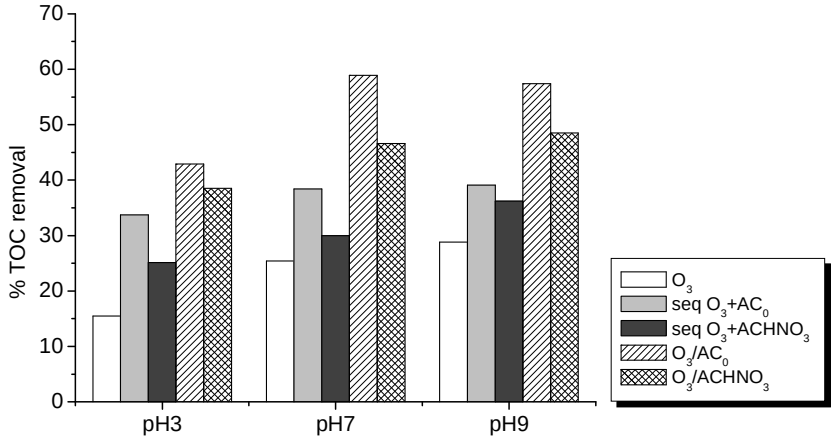

Figure 4.3 TOC removal obtained by ozonation, ozonation in the presence of AC_0 and $ACHNO_3$ and sequential experiments of ozonation and adsorption in AC_0 and $ACHNO_3$.

According to the results depicted in Figure 4.3, there is a significant synergic effect between ozone and activated carbon. Regardless of the pH of the solution, a higher TOC removal is obtained when aniline is ozonised in the presence of activated carbon, comparatively to the sum of the sequential contributions of ozonation and adsorption steps. Regarding the properties of the activated carbon, better results are achieved with the most basic activated carbon. Additionally it is observed that sample $ACHNO_3$ has a smaller adsorption capacity towards aniline single ozonation by-products. Assuming that after 30 min of reaction, the oxidation products remaining in the solution are less reactive towards ozone and less prone to activated carbon adsorption, the increase in TOC removal obtained when ozone and activated carbon are used simultaneously is due not only to its adsorption capacity but also to a catalytic contribution leading to higher rates of mineralisation.

4.4 Conclusions

Ozonation is an efficient process for the removal of aniline from aqueous solution, though leading to the formation of several by-products. Nitrobenzene, *o*- and *p*-aminophenol were three of the detected primary ozonation products of aniline. These products were also easily oxidized by ozone. The rate of aniline removal by single ozonation was observed to be nearly independent of the solution pH. During ozonation in the presence of activated carbon, the rate of aniline decay was higher at pH 7 and 9 than at pH 3. In general, the addition of activated carbon to the ozonation process improves the rate of removal of both aniline and primary oxidation by-products. Consequently, the removal of TOC is significantly improved, when compared to single ozonation. Higher mineralisation rates are obtained at neutral and basic pH. Clearly, the use of basic activated carbons is advantageous for this process, which might be due both to their enhanced ability to catalyse the decomposition of ozone in aqueous phase and to their adsorption capacity towards organic compounds.

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5 Activated Carbon Catalytic Ozonation of Oxamic and Oxalic Acids[1,2]

The oxidation of hazardous organic compounds leads to the formation of several by-products, being oxalic acid and oxamic acid final oxidation products refractory to ozonation. The present work aimed to study the ozonation of those carboxylic acids in the presence of activated carbon at different solution pH. For comparative purposes, experiments of adsorption on activated carbon, ozonation, and ozonation in the presence of activated carbon were carried out. In order to clarify the reaction mechanism, some experiments were done in the presence of a radical scavenger. With the aim of evaluating the role of the activated carbon surface chemistry during the ozonation, two activated carbon samples were assessed. A significant synergistic effect between ozone and activated carbon was evidenced in the oxidation of oxalic acid. Oxamic acid was found to be refractory to oxidation at pH 7. On the other hand, at pH 3, the mineralisation of oxamic acid was significantly enhanced by the presence of activated carbon. Generally, the presence of activated carbon during ozonation increased the rate of degradation of both carboxylic acids leading to mineralisation. Best results were achieved with the most basic activated carbon. In both cases, the efficiency of activated carbon promoted ozonation decreases with the increase of solution pH.

5.1 Introduction

Ozonation processes have been widely and successfully used in the fields of water and wastewater treatments. More recently, the combination of ozone with homogeneous or heterogeneous catalysts in order to activate the decomposition of ozone or improve ozone reactions with several organic compounds has been

[1] Based on PCC Faria, JJM Órfão, MFR Pereira, Appl Catal B Environ 79 (2008) 237–243.

[2] Additional data presented in Appendix D.

investigated [1, 2] and is still subject of intense research. Heterogeneous catalytic ozonation aims to enhance removal of more refractory compounds through the transformation of ozone into more reactive species and/or through adsorption and reaction of the pollutants on the surface of the catalyst. Although supported transition metals are trendy catalysts in ozonation processes, activated carbon (AC) itself has been found to be an attractive and promising alternative to the treatment of wastewaters containing dyes or other organic contaminants [3-9], including carboxylic acids [10, 11].

Activated carbon is believed to promote the decomposition of aqueous ozone [12-16], leading to the formation of oxygenated active species that are responsible for enhancing the mineralisation of organic compounds.

The ozonation of several hazardous organic compounds such as pesticides, dyes, aromatic hydrocarbons, etc, originates significant amounts of saturated organic compounds such as aldehydes, ketones and carboxylic acids. Due to the low reactive nature towards ozone, short chain carboxylic acids tend to accumulate in solution. Hence, single ozonation is not sufficient to achieve a high mineralisation degree.

Oxalic acid has been identified as one of the most common final oxidation products from organic compounds degradation. The oxidation of organic compounds containing nitrogen functional groups can also result in the formation of oxamic acid [17, 18] which is apparently more refractory to oxidation than oxalic acid. The low reaction rate constants reported in the literature for the ozonation of oxalic acid and their corresponding anions ($k < 0.04\ M^{-1}\ s^{-1}$ at pH > 5 [19]) explain why such compounds always accumulate as final products when organic aqueous solutes are ozonised in water. The compounds of low reactivity towards ozone may be oxidized by secondary oxidants such as hydroxyl radicals produced during the decomposition of ozone in aqueous solution. In fact, oxalic acid reacts with $HO^{\cdot}$ radicals at a much higher rate ($k \approx 10^6\ M^{-1}\ s^{-1}$ [20]).

While studying the ozonation of aniline, benzenesulfonic and sulfanilic acids, oxalic acid was identified, as one of the final oxidation products. In the case of aniline and sulfanilic acid, also oxamic acid was detected. These compounds were responsible for great part of the final amount of total organic carbon (TOC) in solution. In this work, the activated carbon promoted ozonation of oxamic and oxalic acid was investigated. Although some data on the ozonation of oxalic acid in

the presence of activated carbon has already been described in the literature [10], as far as we know, information on oxamic acid catalytic ozonation has not yet been presented. It is known that both textural and surface chemical properties control the decomposition of ozone in water [14, 16]. The main goal was to study the catalytic ozonation of these two acids, in order to clarify the reaction mechanism and understand the influence of the activated carbon surface chemistry. In this work, the performance of two activated carbon samples, differing mainly in their chemical surface properties, is compared in the adsorption and catalytic ozonation of two carboxylic acids (oxalic and oxamic acids), which are common final oxidation by-products in the ozonation of organic pollutants. As pH values influence not only ozone decomposition in aqueous solutions, but also surface properties of activated carbon and dissociation of organic molecules in water, two level of pH were studied.

5.2 Experimental

5.2.1 Materials

Oxalic acid (99%) and oxamic acid (96%) were obtained from Sigma-Aldrich. A commercial activated carbon, Norit GAC 1240 PLUS (sample AC_0), was submitted to an oxidation treatment in the liquid phase with HNO_3 6 M under boiling temperature during 3 h (sample $ACHNO_3$) [14] (see chapter 2). The textural characterization of the materials was based on the N_2 adsorption isotherms determined at 77 K. The surface chemistry of the activated carbon samples was characterised by the determination of acidity and basicity, pH_{pzc}, and temperature-programmed desorption (TPD), as described elsewhere [21]. No major differences were observed regarding the textural properties of the activated carbon samples [22]. Sample AC_0 has a BET surface area of 909 m^2/g. It is a fairly basic activated carbon with a pH_{pzc} of 8.5. Sample $ACHNO_3$ has a BET surface area of 827 m^2/g and pH_{pzc} of 3.0. A more detailed characterization of these materials is reported elsewhere [14] (see chapter 2).

5.2.2 Kinetic experiments

The removal of oxalic and oxamic acids from aqueous solutions at different pH values was investigated in a slurry lab-scale reactor equipped with agitation and recirculation jacket (see Appendix A). For comparative purposes, both adsorption on activated carbon and ozonation experiments in the absence of activated carbon were performed in the same system, under identical experimental conditions. Two activated carbons with different surface chemistries were assessed. The reactions were carried out at the natural pH of the acids solutions, which was approximately 3 in both cases, and at pH 7. In the latter case, a phosphate buffer solution (0.01 M) was used to maintain the solution pH. In each experiment the reactor was filled with 700 mL of acid solution 1 mM at the desired pH. In the adsorption and catalytic ozonation experiments, 350 mg of activated carbon (ground to a particle size = 100 - 300 μm) were introduced in the reactor. Ozone was produced from pure oxygen in a BMT 802X ozone generator. The experiments were performed at constant gas flow rate (150 cm^3 min^{-1}, measured at room T and P) and constant inlet ozone concentration (50 g Nm^{-3}). The concentration of ozone in the gaseous phase was monitored with a BMT 964 ozone analyzer. Ozone in the gas phase leaving the reactor was removed in a series of gas washing bottles filled with iodide potassium solution. The agitation was maintained constant at 300 rpm in order to keep the reactor content perfectly mixed and the temperature was set to 25 ºC.

The concentration of both oxalic and oxamic acids was followed by HPLC using a Hitachi Elite Lachrom HPLC equipped with a diode array detector. The stationary phase was a YMC Hydrosphere C18 column (250 mm x 4.6 mm) working at room temperature, under isocratic elution with a mixture of water, acetonitrile and *o*-phosphoric acid at pH 2. The degree of mineralisation was followed by TOC analysis in a Shimadzu TOC-5000A Analyzer. Ammonium ion concentration was measured with a WTW NH500 ammonia-selective electrode.

5.3 Results and discussion

5.3.1 Adsorption of oxalic and oxamic acids on activated carbon

It is understood that the surface chemistry of activated carbon plays a role in the decomposition of ozone in water into more reactive species [14, 16]. Moreover, when working with organic compounds, it is expected that the adsorption capacity

of the carbon samples towards these compounds also plays a key role during activated carbon promoted ozonation. On one hand, adsorption competes with the oxidation reaction to the removal of pollutants from the aqueous phase. On the other hand, the adsorption step may play a role in the mechanism of catalytic ozonation. For these reasons, adsorption studies of oxamic and oxalic acids were carried out separately on both activated carbon samples at different solution pH. The corresponding kinetic results are depicted in Figure 5.1 and Figure 5.2.

At the natural solution pH, which is around 3, approximately 19% of the oxamic acid is adsorbed on AC_0 after 120 minutes, while less than 5% is adsorbed on sample $ACHNO_3$. Figure 5.1 also shows that at neutral pH, oxamic acid adsorption is negligible, especially on sample $ACHNO_3$.

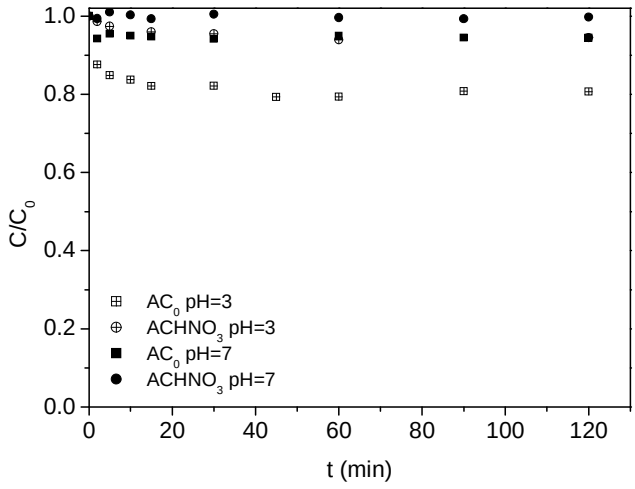

Figure 5.1 Adsorption of oxamic acid on AC_0 and $ACHNO_3$ at different pH (C_0 = 1mM; AC = 0.5 g/L).

Similarly to oxamic acid, oxalic acid uptakes are higher at pH 3 than at pH 7, regardless the nature of the activated carbon. As shown in Figure 5.2, at pH 3 there is a huge difference in the behaviour of both activated carbon samples. After 120 minutes, sample AC_0 adsorbs 38% of oxalic acid from solution, while, in the same conditions, sample $ACHNO_3$ removes only 9% of it.

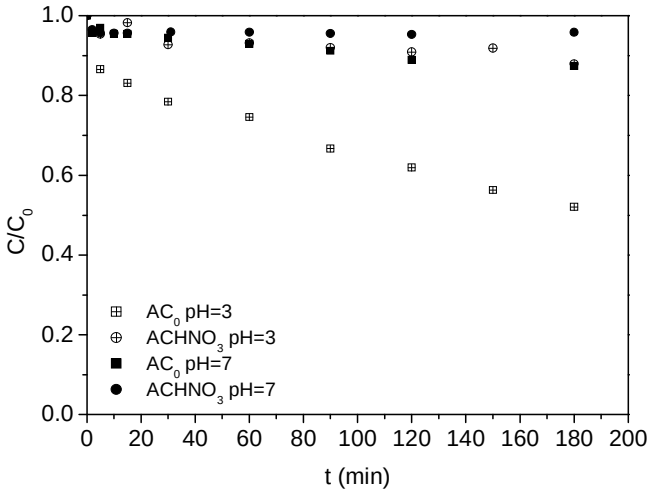

Figure 5.2 Adsorption of oxalic acid on AC_0 and $ACHNO_3$ at different pH (C_0 = 1 mM; AC = 0.5 g/L).

The fact that both acids are better adsorbed at acidic pH than at neutral pH might be due, to a great extent, to the different species present in water, which have different hydrophilicity. Significant changes in solubility are observed with pH variation for organic acids and bases. Depending on the solution pH, those might be in the molecular or ionic form. Since charged solutes are able to strongly interact with water, the charged form of an acid or base can be much more hydrophilic, thus being less prone to be adsorbed on activated carbon. For oxalic acid (pKa_1 = 1.23; pKa_2 = 4.19), increasing pH results in an increase in the fraction of ionic species, as the acid deprotonates to form the conjugated base. The increase in the pH leads to an increase in the hydrophilicity of the dissolved species (the common logarithm of the distribution coefficient K_{ow} decreases from -1.92 to -8.73 when pH increases from 3 to 7). As a consequence, the dissolved species may have a much lower affinity towards activated carbon surface at pH 7.

Oxamic acid molecule has a basic and an acid functional group (pKa_1 = 2.5 for the carboxylic group and pKa_2 = 11.8 for NH_3^+) [17]. According to this, at pH 3 dissolved oxamic acid is approximately equally distributed in the following species: $HOOC\text{-}CONH_3^+$ and $^-OOC\text{-}CONH_3^+$, while at pH 7 the latter species predominates in solution. The presence of both charged groups highly increase the hydrophilicity

of the oxamic acid, which may explain the lower adsorption on activated carbon at pH 7.

Another possible explanation for the decrease in both acid uptakes when pH increases is the presence of phosphate ions in solution, necessary to buffering, which may compete with both oxalic and oxamic acid for adsorption on the activated carbon surface. Actually, it was observed that at pH 3 the adsorption of oxamic acid on sample AC_0 slightly decreased when it was carried out in the presence of a phosphate solution, confirming the interference of the phosphate buffer solution during adsorption.

It was also observed that, regardless of the pH, sample AC_0 always presented higher adsorption capacity than sample $ACHNO_3$. At pH 3, the surface of sample AC_0 is positively charged (pH_{pzc} > pH) while sample $ACHNO_3$ has a neutral net charge surface. Thus, anionic species in solution have higher affinity to activated carbon AC_0 due to electrostatic interactions. At pH 7, $ACHNO_3$ surface becomes negatively charged (pH_{pzc} < pH) increasing electrostatic repulsive interactions between the carbon surface and anionic species in solution. This is valid especially for oxalic acid that at pH 7 is totally deprotonated. The results obtained are consistent with what has been stated for the adsorption of organic compounds [23]. In general, basic carbons such as sample AC_0 present better adsorption capacities than more acidic ones when solutes are present either in their molecular or anionic form.

5.3.2 Ozonation of the selected carboxylic acids

The removal of dissolved oxamic and oxalic acids by ozonation in the presence or absence of activated carbon was studied separately at pH 3 (natural pH of the solutions) and pH 7 (buffered solutions).

5.3.2.1 Oxamic acid

Oxamic acid was shown to be highly refractory towards ozonation at pH 3. According to Figure 5.3, the addition of a small amount of activated carbon resulted in a major increase in the removal of oxamic acid from solution.

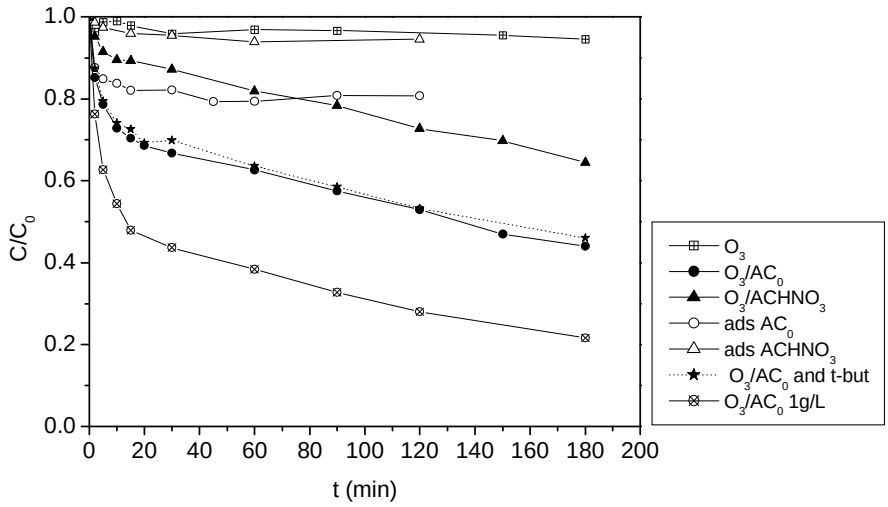

Figure 5.3 Evolution of the dimensionless concentration of oxamic acid at pH 3; influence of the concentration of AC_0 and influence of the presence of *tert*-butanol (C_0 = 1 mM, AC = 0.5 g/L or 1 g/L, $C_{tert\text{-butanol}}$ = 10 mM).

The degree of mineralisation is also an important parameter to monitor in this type of oxidation processes, as it represents a measure of the removal of organic matter from water. In this work, the mineralisation was checked by measuring the total organic carbon (TOC) of the solution along time. The TOC concentration determined experimentally was in good agreement, within the experimental error, with that calculated from the residual oxamic acid concentration during ozonation (see Appendix D), and was consistent with the absence of organic intermediates in the HPLC chromatograms. During activated carbon promoted ozonation, oxamic acid is mutually adsorbed and mineralised. According to the literature, the ozonation of $-NH_2$ containing compounds might lead to the formation of NO_3^- or /and NH_4^+. The concentration of NH_4^+ was checked during the ozonation of oxamic acid at pH 3, in the presence of 0.5 g/L of sample AC_0. After 180 min of reaction, the amount of NH_4^+ detected in solution represented no more than 15% of the converted oxamic acid. Under the experimental conditions used, no measurable NO_3^- concentrations were noticed. Part of the ammonia formed is thought to be either adsorbed on the activated carbon and/or converted into N_2. In fact, these possibilities have been considered by Aguilar et al. [24], who reported the

elimination of aqueous ammonia by wet air oxidation using activated carbon as catalyst. Additionally, the ozonation of an aqueous solution of ammonia (C_0 = 0.5 mM) was carried out in the presence of activated carbon, and a reduction of 14% of the initial NH_4^+ concentration was registered after 180 min of reaction. Neither NO_2^- nor NO_3^- were detected in the course of the reaction. One might also consider the possibility of formation of other gaseous nitrogen compounds (e.g. nitrogen oxides) during the oxidation of oxamic acid on the surface of the activated carbon.

Adsorption results, previously discussed, showed that removal of oxamic acid by adsorption on sample $ACHNO_3$ was quite low. Nonetheless, the combination of O_3 and $ACHNO_3$ resulted in a significant increase in the removal of oxamic acid. These observations are important to reinforce the existence of a significant synergistic effect between ozone and activated carbon. In this case the result obtained is more than just a sum of the two contributions (ozonation and adsorption); thus the oxidation of oxamic acid can be attributed to a catalytic effect. The difference observed between the results obtained with samples AC_0 and $ACHNO_3$ could be correlated to the role of the surface chemistry of the activated carbon on the ozone decomposition [14] and/or to the higher adsorption capacity of sample AC_0 in opposition to $ACHNO_3$.

As far as activated carbon catalytic ozonation is concerned, Jans and Hoigné [15] reported that the decomposition of ozone in water in the presence of an activated carbon or a carbon black, yields hydroxyl radicals in the aqueous phase. In order to look ahead relatively to the mechanism of oxamic acid catalytic ozonation, an experiment was carried out in the presence *tert*-butanol (C = 10 mM), a well known hydroxyl radical scavenger, which has been reported not to significantly adsorb on activated carbon [10]. *Tert*-butanol reacts very rapidly with hydroxyl radicals ($k = 5 \times 10^8$ M^{-1} s^{-1}) [25] and very slowly with ozone ($k = 0.03$ M^{-1} s^{-1}) [26]. As shown in Figure 5.3, the ozonation of oxamic acid catalysed by AC_0 was not influenced by the presence of *tert*-butanol. Assuming that this alcohol is an effective $HO^{\bullet}$ radical scavenger, and knowing that oxamic acid is not oxidized by direct ozonation, it can be concluded that, under these conditions, the oxidation of oxamic acid occurs mainly trough reactions on the surface of the activated carbon. This fact would also explain why sample $ACHNO_3$ has a smaller activity in this reaction. Due to the high amount of oxygenated surface groups, which have an electron withdrawing effect, sample $ACHNO_3$ has a lower electron density when compared to sample AC_0. As a result, both oxamic acid and ozone molecules have less affinity towards sample

$ACHNO_3$. As shown in Figure 5.3, the increase in activated carbon amount from 0.5 g/L to 1 g/L had a positive effect in the oxidation of oxamic acid, thus reinforcing the importance of the available surface area in the reaction mechanism.

The influence of the presence of a phosphate buffer solution, used in the experiments at pH 7, was tested in the ozonation of oxamic acid in the presence of AC_0 at pH 3. As can be observed in Figure 5.4, the presence of the mentioned phosphate solution not only decreased adsorption (as previously reported) but had also a significant effect on the catalytic ozonation of oxamic acid. According to the previous reasoning, it is probable that the decrease in the oxidation rate of oxamic acid is mainly due to the fact that phosphate ions compete with oxamic acid and ozone towards adsorption on activated carbon surface, weakening its catalytic effect.

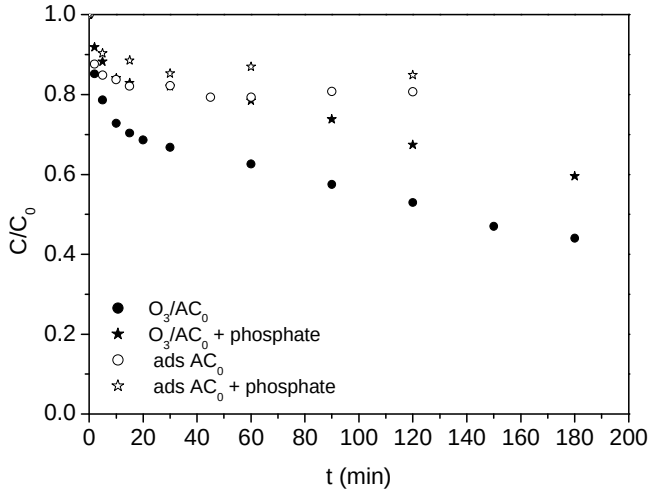

Figure 5.4 Influence of the phosphate solution on the evolution of the dimensionless concentration of oxamic acid at pH 3 (C_0 = 1 mM, AC = 0.5 g/L).

Oxamic acid was found to be refractory to single ozonation at pH 7 (Figure 5.5). This observation was not predictable since ozone self-decomposition into oxygen radical species is initiated by the presence of HO^- ions [27]. As discussed before, this effect is believed to be enhanced in the presence of activated carbon. Nevertheless, at this pH, single ozonation of oxamic acid resulted in a removal of

only 2% after 120 minutes of reaction. In addition, the adsorption of this acid on samples AC_0 and, particularly, $ACHNO_3$ was negligible, as discussed in the previous section.

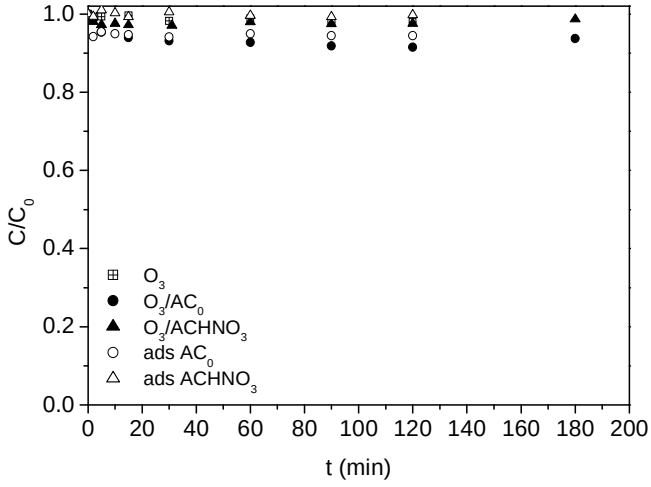

Figure 5.5 Evolution of the dimensionless concentration of oxamic acid at pH 7 (C_0 = 1 mM, AC = 0.5 g/L).

In this case, the addition of activated carbon to the process was not effective and the increase observed in the removal of oxamic acid was mainly due to the contribution of adsorption. Similar results were obtained during the ozonation in the presence of AC_0 at higher pH (see Appendix D). Apparently, at neutral and basic pH, oxamic acid is highly resistant both to molecular ozone and hydroxyl radicals attack and is not significantly oxidized. At this range of pH, oxamic acid is mainly present as a zwitterion ($^-OOC\text{-}CONH_3^+$), which is highly hydrophilic, and stable in water. According to Leitner et al. [17], who studied the removal of oxamic acid with γ-irradiation, this fact and the absence of C-H bonds explains its small reactivity towards $HO^\cdot$ radicals. Even though oxamic acid can be mineralised by $HO^\cdot$ radicals, at neutral pH, its oxidation requires a 100 times higher $HO^\cdot$ dosage than most of the organic compounds [17].

5.3.2.2 Oxalic acid

The ozonation of oxalic acid (C_0 = 1mM) was carried out at pH 3 in the first place. The results obtained are depicted in Figure 5.6.

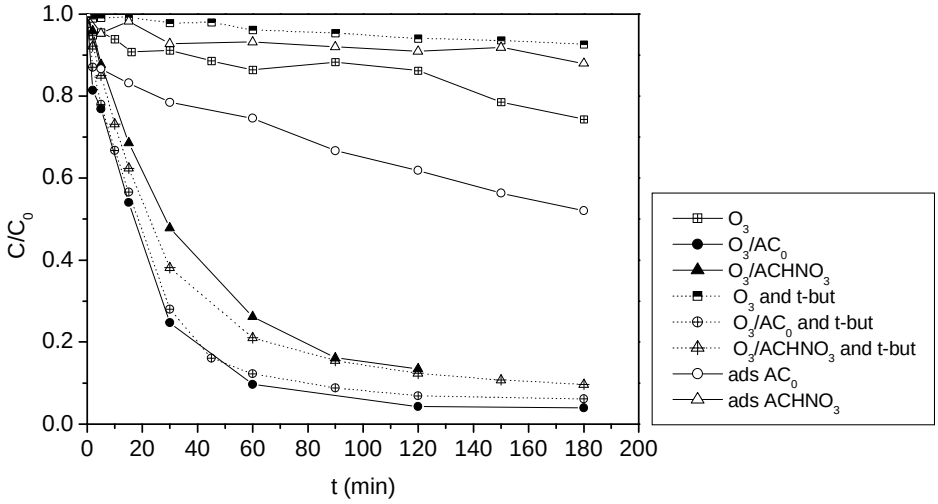

Figure 5.6 Evolution of the dimensionless concentration of oxalic acid at pH 3 (C_0 = 1 mM, AC = 0.5 g/L, $C_{tert\text{-butanol}}$ = 10 mM).

It was observed that the mineralisation of oxalic acid was significantly enhanced by the addition of activated carbon. The simultaneous use of ozone and activated carbon resulted in the removal of 92% and 86% of dissolved oxalic acid, after 120 minutes, for samples AC_0 and $ACHNO_3$, respectively. Thus, a significant synergistic effect between ozone and activated carbon is evidenced in the oxidation of oxalic acid. As expected, samples AC_0 and $ACHNO_3$ originated different results, which could be explained by a sum of two effects: AC_0 has a higher adsorption capacity towards oxalic acid than sample $ACHNO_3$ and a superior capability to enhance the catalytic decomposition of ozone into surface radical species and/or oxygen containing radicals, such as $HO^{\bullet}$, in solution. The ozonation of oxalic acid in the presence of AC_0 at pH 3 was not considerably affected by the presence of the radical scavenger *tert*-butanol (Figure 5.6), and similar results were obtained with sample $ACHNO_3$. This leads to the conclusion that, at these conditions, the catalytic ozonation of oxalic acid occurs mainly on the surface of the activated carbon, and is

not a direct result of a higher concentration of hydroxyl radical species in solution. These results are not in agreement with those reported by Beltrán et al. during the activated carbon promoted ozonation of oxalic acid at pH 2.5 [10], where the presence of *tert*-butanol significantly inhibited the oxidation rate of oxalic acid compared to the activated carbon catalytic ozonation without the radical scavenger.

The ozonation of oxalic acid leads directly to mineralisation, i.e., there is no formation of organic intermediates. Therefore, total organic carbon concentration determined experimentally ought to be in agreement with that calculated from residual concentration of the oxalic acid. This was consistent with the results obtained in this investigation (see Appendix D).

Similarly to what happened at pH 3, the simultaneous use of ozone and activated carbon at pH 7 is definitely advantageous for the oxidation of oxalic acid. According to the results depicted in Figure 5.7, oxalic acid elimination increased up to 69 or 90%, after 120 minutes of reaction, when respectively samples $ACHNO_3$ or AC_0 were used during ozonation reactions.

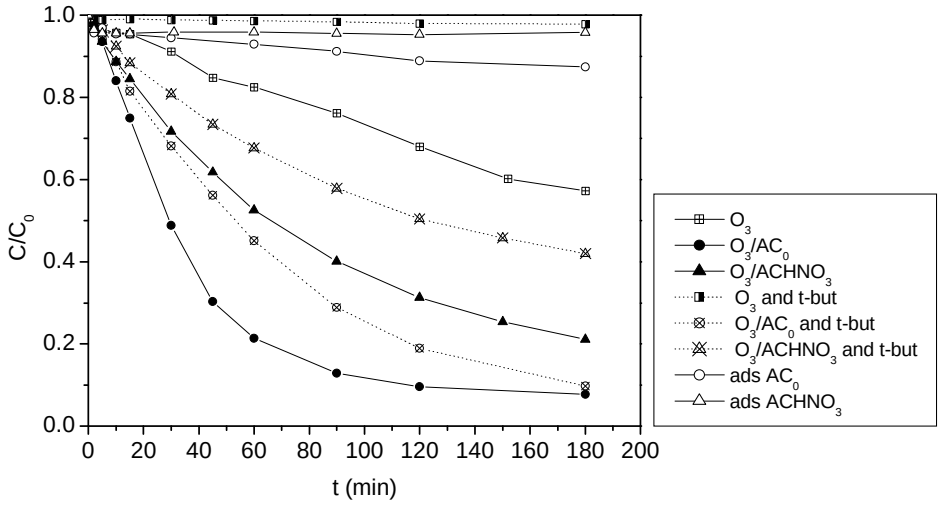

Figure 5.7 Evolution of the dimensionless concentration of oxalic acid at pH 7 (C_0 = 1 mM, AC = 0.5 g/L, $C_{tert\text{-butanol}}$ = 10 mM).

In conformity with the mechanism for ozone decomposition in water, the increase in pH leads to a faster decomposition of ozone into oxygen radical species leading to the formation of $HO^{\cdot}$ radicals. Actually, when comparing experimental data on oxalic acid single ozonation, at the two pH values studied, a higher removal rate was observed at pH 7. When single ozonation was carried out in the presence of *tert*-butanol, almost no oxalic acid mineralisation was observed, which confirms that the homogeneous oxidation of oxalic acid practically only occurs via $HO^{\cdot}$ radicals.

Contrary to what happened at pH 3, it was observed that the presence of *tert*-butanol inhibits the catalytic ozonation of oxalic acid comparatively to the same reaction without *tert*-butanol (Figure 5.7).

This effect was observed for AC_0 and $ACHNO_3$. This suggests that the reaction mechanism involves the formation of hydroxyl radicals that are scavenged in the presence of *tert*-butanol, resulting in a decrease of the ozonation rate of oxalic acid. Simultaneously, surface reactions are assumed to occur as well. In conclusion, the experimental results suggest two different pathways in the catalytic ozonation of oxalic acid in the presence of activated carbon: one occurs on the surface of the activated carbon, involving adsorption, surface reaction and desorption steps; the other occurs in the bulk liquid, involving reactions between highly oxidant species, resulting from ozone decomposition, and dissolved oxalic acid.

When comparing the results from ozonation in the presence of AC obtained at both pH 3 and 7, it is clear that better results are achieved at acidic pH. It is known that the pH not only influences ozone decomposition in aqueous solutions, but also controls the surface properties of activated carbon and the dissociation of organic molecules in water. As said before, a higher pH accelerates the decomposition of ozone into more reactive species that are likely to participate in the mechanism of oxalic acid oxidation. However, at acidic conditions oxalic acid has a higher affinity towards activated carbon than at higher pH, as previously explained. Therefore, adsorption seems to represent an important path in the activated carbon catalytic ozonation of carboxylic acids.

5.3.3 Reaction mechanism

According to the experimental results obtained in this work there is strong evidence that the ozonation of both carboxylic acids occurs through a catalytic mechanism involving surface and bulk reactions. It is visible that, at pH 7, hydroxyl radicals are partially responsible for the mineralisation of oxalic acid in solution. Due to this evidence and to the high instability of ozone in water, which decomposes through a radical chain mechanism, homogeneous oxidation reactions have to be considered.

Regarding the decomposition of ozone in aqueous solution, it is established that it is initiated by the presence of HO^- ions; so pH plays a major role in this process:

$$O_3 \xrightarrow{HO^-} HO^\bullet \quad (5.1)$$

As said before, several authors have reported that activated carbon accelerates the decomposition of ozone [12-16]. It is consensual that both textural and surface chemical properties influence that decomposition, but doubts on the mechanism still remains. According to the literature, two possible pathways can explain the decomposition of O_3 in the presence of activated carbon. The first one assumes that activated carbon acts as an initiator of the decomposition of ozone yielding free radical species, such as $HO^\bullet$ in solution [15]:

$$O_3 \xrightarrow{AC} HO^\bullet \quad (5.2)$$

Another possibility is the adsorption and reaction of ozone molecules on the surface of the activated carbon, yielding surface oxygenated radicals [12]:

$$O_3 + AC \rightarrow AC - O \quad (5.3)$$

where AC-O stands for any oxygen-containing active species on the surface of the activated carbon, including $HO^\bullet$ radicals. The oxidation of carboxylic acids is thus possible to occur on the surface of the activated carbon, between the adsorbed reagent (R) and surface radical species, according to the following steps:

$$R + AC \rightarrow AC - R \quad (5.4)$$

$$AC - R + AC - O \rightarrow P \quad (5.5)$$

As this mechanism has no experimental evidence, it is necessary to consider that adsorbed species might also react with dissolved ozone, reaction (5.6), or hydroxyl radicals from the aqueous phase, reaction (5.7). Similar assumptions have been

presented by Beltrán et al [28], concerning the ozonation of pyruvic acid catalysed by activated carbon.

$$AC - R + O_3 \rightarrow P \quad (5.6)$$

$$AC - R + HO^{\bullet} \rightarrow P \quad (5.7)$$

As already mentioned, the rate constant of the reaction between carboxylic acids and molecular ozone is quite low. The oxidation of these species in aqueous solution occurs via a radical chain mechanism where $HO^{\cdot}$ radicals are the main intervenient. Therefore, a homogeneous reaction mechanism must be considered too:

$$R + HO^{\bullet} \rightarrow P \quad (5.8)$$

As shown in Figure 5.3 and Figure 5.6, the presence of the radical scavenger (*tert*-butanol) did not inhibit the oxidation of oxamic and oxalic acids at pH 3. Therefore, at those conditions, both reactions (5.7) and (5.8) are not likely to occur. At pH 7 the existence of a reaction path involving $HO^{\cdot}$ radicals was experimentally evidenced in oxalic acid catalytic ozonation. Even so, this mechanism does not explain the results obtained for oxamic acid at pH 7, which are probably related to the chemical nature of this compound.

Steps (5.2), (5.3) and (5.4) entail the dependence of the proposed mechanism on the surface properties of the activated carbon, as it influences both adsorption of reactants and interaction with ozone molecules, as previously explained.

5.4 Conclusions

The simultaneous use of ozone and activated carbon yields significant increases of oxalic and oxamic acid removal from water when compared to single ozonation and single adsorption, proving the existence of a catalytic reaction mechanism. Exception was observed for oxamic acid, as it was found to be resistant to oxidation at neutral and basic pH. Generally, the presence of activated carbon during ozonation increases the rate of degradation of both carboxylic acids leading to mineralisation. A higher basicity of the activated carbon enhances the efficiency of this treatment process.

The low reactivity of these compounds towards direct ozonation and the non-existent influence of the radical scavenger at pH 3 suggest that the oxidation occurs

mainly through reactions on the surface of the activated carbon. In the case of oxalic acid at pH 7, the results can be explained from a mechanism involving both surface reactions and bulk reactions between the organic solute and hydroxyl radicals.

For both carboxylic acids, the efficiency of activated carbon promoted ozonation decreases with the increase of solution pH. At least in part, this might be related to a higher solubility of solutes at neutral and basic conditions, and to a consequent lower affinity towards activated carbon surface.

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6 Catalytic Ozonation of Sulfonated Aromatic Compounds in the Presence of Activated Carbon[1]

The ozonation of two model aromatic compounds, benzenesulfonic acid and sulfanilic acid, was carried out in the presence of activated carbon. With the aim of evaluating the role of the activated carbon surface chemistry during the ozonation, two activated carbon samples were assessed. Activated carbon promoted ozonation increased the rate of elimination of the selected aromatic compounds and, most of all, enhanced the removal of organic matter. Selected experiments were carried out in the presence of a radical scavenger, which evidenced the participation of $HO^{\cdot}$ radicals in the oxidation mechanism during the degradation of benzenesulfonic acid, and in the mineralisation of the oxidation by-products. No significant similar effect was observed in the degradation of sulfanilic acid. The mineralisation of the organic compounds in solution is due to a complex mechanism involving adsorption, and direct and indirect ozone reactions, occurring both in the liquid phase and on the activated carbon surface. Regardless of its nature, activated carbon acts as a catalyst in the ozonation reaction, though best results are achieved with the most basic activated carbon sample.

6.1 Introduction

Sulfonated aromatic compounds as well as aromatic amines are released into the environment in large amounts, mainly through the discharge of industrial effluents. Aromatic sulfonates are used in the production of azo dyes, drugs, detergents, etc [1]. Production and biodegradation of dyestuffs, represent one of the main sources of these recalcitrant pollutants, especially azo dyes, which is one of the largest class of dyes applied in textile processing [2]. Generally, textile effluents are treated through conventional biological processes. The biodegradation of azo dyes may

[1] Based on PCC Faria, JJM Órfão, MFR Pereira, Appl Catal B Environ 83 (2008) 150–159.

proceed in two stages. The first one involves the reductive cleavage of $-N=N-$ moieties in anaerobic conditions, resulting in the formation of hazardous aromatic amines, such as aminobenzenesulfonic acids. The second path involves the aerobic degradation of the latter compounds. Sulfonated aromatic amines constitute a group of aromatic compounds particularly difficult to degrade. Many of those formed during the reduction of sulfonated azo dyes are not susceptible to anaerobic or aerobic biodegradation, and conventional biological treatments fail to mineralise most of these compounds [1, 2]. The organosulfonate group plays an important role in altering the solubility and dispersion properties of the molecule and increases its refractory character to biodegradation due to the thermodynamic stability of the carbon-sulfur bond [3]. Consequently, effluents from dyehouses and textile industries are often contaminated with sulfonated aromatic compounds. Chemical oxidation processes may be used as an alternative and/or as a complement to biological treatments, in order to accomplish a faster and higher mineralisation of these compounds.

Ozonation and catalytic ozonation processes have been widely studied in the scope of wastewater treatments. Heterogeneous catalytic ozonation aims to enhance removal of more refractory compounds through the transformation of ozone into more reactive species and/or through adsorption and reaction of the pollutants on the surface of the catalyst. Different supported and unsupported catalysts have been tested in the ozonation of several organic compounds [4]. Among the studied materials, activated carbon (AC) has been found to be an attractive alternative to the treatment of wastewaters containing dyes or other organic contaminants [5-11]. Recently, the removal of naphtalenesulfonic compounds from aqueous solutions has been successfully accomplished by ozonation in the presence of activated carbon [7]. Activated carbon is believed to promote the decomposition of aqueous ozone [12-16], leading to the formation of oxygen active species both in the liquid phase and on the carbon surface, that are responsible for enhancing the mineralisation of organic compounds.

In this work, two aromatic sulfonated compounds, sulfanilic acid and benzenesulfonic acid, were selected as model compounds. The main goal was to study the catalytic ozonation of these two aromatic acids, in order to clarify the reaction mechanism and understand the influence of the activated carbon surface chemistry on the removal of those compounds, and on the mineralisation of the corresponding solutions. The most significant final oxidation products detected

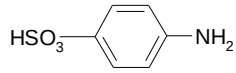
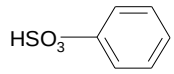
were also followed along time. As pH values influence not only ozone decomposition in aqueous solution [14], but also surface properties of activated carbon [17] and dissociation of organic molecules in water, two level of pH were studied.

6.2 Experimental

6.2.1 Materials

Sulfanilic acid (SA) and benzenesulfonic acid (BSA) were obtained from Sigma-Aldrich. Some properties of these compounds are presented in Table 6.1.

Table 6.1. Properties of the selected aromatic compounds.

Solute		M (g/mol)	pKa
Sulfanilic Acid (SA)		173.2	2.92*
Benzenesulfonic Acid (BSA)		158.2	-2.36

* pKa corresponding to the group NH_3^+

A commercial activated carbon, Norit GAC 1240 PLUS (sample AC_0), was submitted to an oxidation treatment in the liquid phase with HNO_3 6 M under boiling temperature during 3 h (sample $ACHNO_3$) [14] (see chapter 2). The textural characterization of the materials was based on the N_2 adsorption isotherms determined at 77 K. The surface chemistry of the activated carbon samples was characterised by the determination of acidity and basicity, pH_{pzc}, and temperature-programmed desorption (TPD), as described elsewhere [18]. No major differences were observed regarding the textural properties of the activated carbon samples [19]. Sample AC_0 has a BET surface area of 909 m^2/g. It is a fairly basic activated carbon with a pH_{pzc} of 8.5. Sample $ACHNO_3$ has a BET surface area of 827 m^2/g and pH_{pzc} of 3.0. A more detailed characterization of these materials is reported elsewhere [14] (see chapter 2).

6.2.2 Ozonation experiments

The removal of sulfanilic (SA) and benzenesulfonic (BSA) acids from aqueous solutions at different pH values was investigated in a slurry lab-scale reactor equipped with agitation and recirculation jacket (see Appendix A). For comparative purposes, both adsorption on activated carbon and ozonation experiments in the absence of activated carbon were performed in the same system, under identical experimental conditions. The two activated carbons mentioned before were assessed. The reactions were carried out at the natural pH of the acids solutions, which was 3.0 for BSA and 3.3 for SA, and at pH 7. In the latter case, a phosphate buffer solution (0.01 M) was used to maintain the solution pH. In each experiment the reactor was filled with 700 mL of acid solution at a concentration of 1 mM and at the desired pH. In the adsorption and catalytic experiments, 350 mg of activated carbon (particle size: 100-300 μm) were introduced in the reactor. In the experiments carried out in the presence of *tert*-butanol, a concentration of 10 mM of this radical scavenger was used. Other experimental conditions and procedures are reported elsewhere [20] (see chapter 5).

The concentrations of both aromatic acids and detected intermediates (oxalic acid, maleic acid, oxamic acid and nitrates) were followed by HPLC using a Hitachi Elite Lachrom HPLC equipped with a diode array detector. The stationary phase was a YMC Hydrosphere C18 column (250 mm x 4.6 mm) working at room temperature. Sulfanilic acid and respective degradation compounds were analysed under isocratic elution with a mixture of water, acetonitrile and *o*-phosphoric acid at pH 2.0. In the case of benzenesulfonic acid, HPLC measurements were done under isocratic elution with a mixture of water, NaH_2PO_4 and *o*-phosphoric acid at pH 2.8. Ammonium ion concentration was measured with a WTW NH500 ammonia-selective electrode. The degree of mineralisation was followed by TOC analysis in a Shimadzu TOC-5000A Analyzer.

6.3 Results and discussion

Kinetic experiments of ozonation in the presence of the activated carbons have been carried out for both compounds at two pH levels. For comparative purposes, experimental data on adsorption and single ozonation are also presented. A detailed study on the adsorption of the selected compounds on the same activated carbon samples has been presented elsewhere [21] (see chapter 3). In the following sections

the results obtained for BSA and SA degradation are presented and discussed separately.

6.3.1 Degradation of benzenesulfonic acid

Benzenesulfonic acid ozonation was first carried out at its natural pH, which is 3.0. Benzenesulfonic acid is a strong acid (pKa = -2.36); therefore, it is in its corresponding deprotonated form both at pH 3 and 7. Under the selected experimental conditions, the single ozonation of BSA led to a complete conversion in approximately 80 min at pH 3.0 (Figure 6.1a). The simultaneous use of ozone and activated carbon enhanced the removal of BSA from solution, and better results were achieved with the fairly basic activated carbon (sample AC_0).

The same trend was observed in terms of TOC removal, reinforcing the importance of the activated carbon in the removal/mineralisation of both BSA and oxidation by-products. During the first 10 minutes of reaction, the ozonation does not lead to any significant TOC removal. In fact, TOC removal observed in this period in the catalytic reaction might be due to adsorption contribution. However, after approximately 15 min, the adsorption apparently tends to a plateau. Even though it is not yet in equilibrium, the decrease in BSA concentration is very small. For longer reaction times there is an evident synergistic effect in the simultaneous use of ozone and activated carbon. The mineralisation rate is significantly improved by the presence of both activated carbon samples, which is not explained by the sum of single ozonation and adsorption contribution. After 180 minutes of reaction the TOC removal achieved with samples AC_0 and $ACHNO_3$ was 83% and 74% respectively, against 51% achieved with single ozonation.

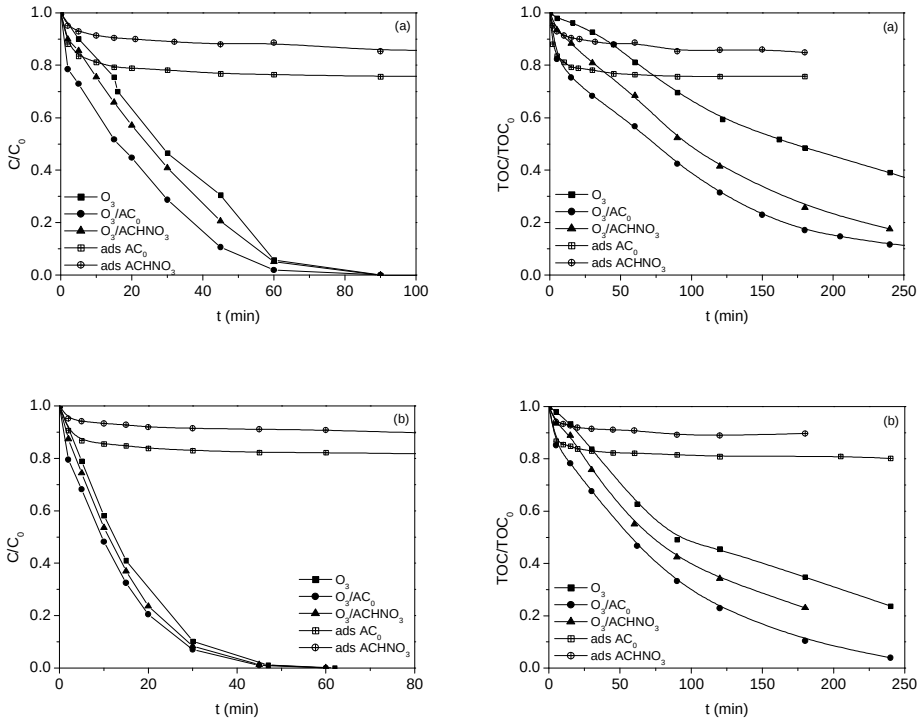


Figure 6.1. Dimensionless BSA and TOC concentrations during adsorption, single ozonation and ozonation of BSA in the presence of AC at pH 3(a) and pH 7 (b); (C_0 = 1 mM, AC = 0.5 g/L).

The ozonation of BSA originates numerous intermediary products which identification was not always possible to accomplish. In this particular case we were interested in identifying final oxidation products highly refractory to ozonation in order to evaluate the role of the activated carbon in their mineralisation. In the case of BSA, oxalic acid was identified as one of the main reaction intermediates that persisted in solution and was monitored during the reaction period. The results obtained are depicted in Figure 6.2. In addition, the mineralisation of aromatic sulfonates results in the release of the sulphur moiety. Accordingly, the ozonation of BSA results in the formation of SO_4^{2-}.

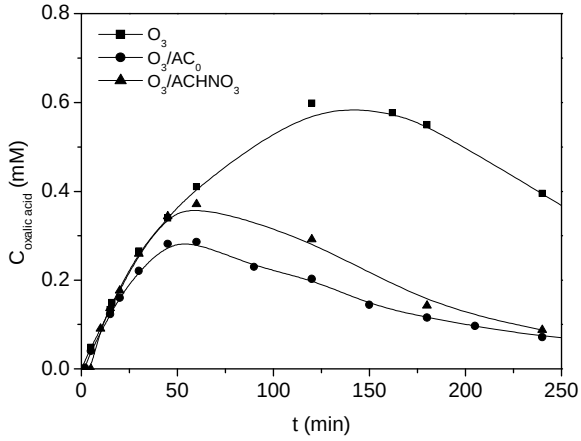


Figure 6.2. Evolution of oxalic acid concentration during catalytic and non-catalytic ozonation of BSA at pH 3 (C_0 = 1 mM, AC = 0.5 g/L).

The low reaction rate constants reported in the literature for the ozonation of oxalic acid and their corresponding anions ($k < 0.04$ M^{-1} s^{-1} at pH > 5) explain why such compounds always accumulate as final products when organic aqueous solutes are ozonised in water [22]. The compounds of low reactivity towards ozone may be oxidized by secondary oxidants such as hydroxyl radicals produced during the decomposition of ozone in aqueous solution. In fact, oxalic acid reacts with $HO^{\cdot}$ radicals with a rate constant of approximately 10^6 M^{-1} s^{-1} [23]. Oxalic acid can also be oxidized through heterogeneous catalytic reactions in the presence of activated carbon or other catalysts [20, 24, 25].

In the experiments carried out, it was observed that the amount of oxalic acid accumulated in solution was always lower when ozonation was carried out in the presence of AC, which clearly indicates an enhancement in the mineralisation of this compound. Therefore, the role of activated carbon in the ozonation of organic compounds becomes crucial in the degradation of oxidation by-products. Sample AC_0 led to lower concentrations of oxalic acid than sample $ACHNO_3$, which is in agreement with the results reported for the ozonation of oxalic acid catalysed by activated carbon [20] (see chapter 5).

The rate of removal of BSA by single ozonation was significantly higher at pH 7 than at pH 3 and complete disappearance of BSA was achieved in ca. 45 min

(Figure 6.1b). This behaviour is in accordance with what was expected, as the increase of solution pH leads to an increase in the ozone self-decomposition originating $HO^{\cdot}$ among other reactive oxygen-containing radical species. Hydroxyl radicals are responsible for the oxidation of a vast number of organic compounds. In this case, the increase in the rate of degradation by single ozonation is attributed to a higher concentration of $HO^{\cdot}$ in solution at pH 7, comparatively to pH 3 where direct ozone reactions predominate.

At pH 7 the simultaneous use of ozone and activated carbon resulted only in a slight increase in the removal rate of BSA. A more distinct effect was observed in terms of TOC removal, especially for sample AC_0 that significantly enhanced the extent of mineralisation. After 180 minutes of reaction the TOC removal achieved with samples AC_0 and $ACHNO_3$ was 90% and 77%, respectively, against 65% attained in single ozonation. The effect of pH is more pronounced in single ozonation than in the presence of activated carbon, where this effect is lessened. Among all the oxidation intermediates present in the reaction samples chromatograms, maleic acid (only trace amounts were observed at pH 3) and oxalic acid were identified and quantified along time. According to Figure 6.3, maleic acid accumulated in solution during the first minutes of reaction and was easily oxidized by ozone. After ca. 45 minutes of reaction no maleic acid was detected.

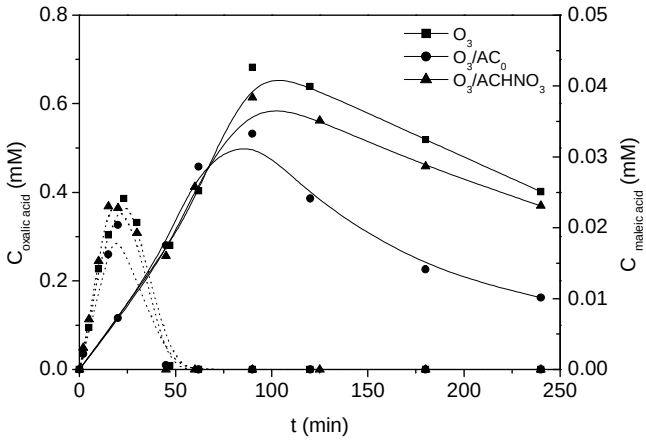


Figure 6.3. Evolution of oxalic acid (solid lines) and maleic acid (dotted lines) concentrations during catalytic and non-catalytic ozonation of BSA at pH 7 (C_0 = 1 mM, AC = 0.5 g/L).

As previously stated, oxalic acid is described in the literature as being refractory to direct ozonation. Nevertheless it is prone to be oxidized by the attack of $HO^{\cdot}$ radicals or by oxidation on the surface of the activated carbon. Figure 6.3 shows that, in the presence of activated carbon, particularly sample AC_0, the concentration of oxalic acid resulting from the oxidation of BSA at pH 7 is lower than that obtained in single ozonation, which implies a faster removal of this compound from water. When comparing the results at both studied pH, it was found that oxalic acid was more efficiently removed at pH 3 than at pH 7. During single ozonation, the evolution of the concentration of oxalic acid was quite similar independently of the solution pH. In the presence of activated carbon, the concentration of oxalic acid is always lower at pH 3 than at pH 7, indicating that the conversion for this compound is higher at acidic pH. These observations are consistent with the results obtained during the study of oxalic acid ozonation promoted by activated carbon [20] (see chapter 5).

In order to better understand the ozonation mechanism of BSA, a few experiments were carried out in the presence of a well know radical scavenger. Due to its $HO^{\cdot}$ radical scavenging action, *tert*-butanol was added to the solution, in order to suppress the reactions in the bulk between the BSA or the corresponding organic by-products, and the $HO^{\cdot}$ radicals. The results obtained at pH 3 and pH 7 are depicted in Figure 6.4.

It was observed that the presence of *tert*-butanol inhibited the removal rate of BSA at both acid and neutral pH. As shown before, the ozonation of BSA is enhanced by an increase in the solution pH, which might be explained by a higher concentration of $HO^{\cdot}$ radicals in solution that contributes to a faster degradation of BSA. This fact, together with the negative impact of the presence of *tert*-butanol in the reaction, evidences that the complete removal of BSA is hardly accomplished only by molecular ozone attack. This provides experimental evidence that even at pH 3 the oxidation of BSA occurs via a radical mechanism involving $HO^{\cdot}$ radicals as main oxidizing species. The ozone attack to the aromatic ring system is highly electrophilic and also highly selective. It is known that the substituent $-HSO_3$ is a strongly deactivating group for that attack, since it decreases the electron density at the *ortho*- and *para*- positions of the ring through a resonance withdrawing effect. Hence these sites are less nucleophilic and therefore, less prone to electrophilic attack by molecular ozone.

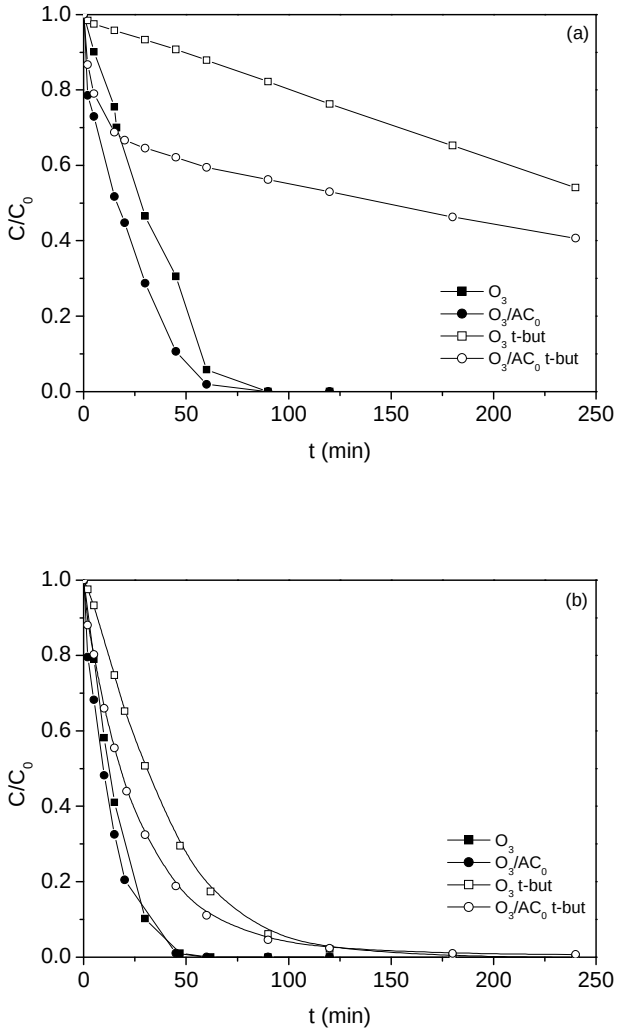


Figure 6.4. Influence of *tert*-butanol on the dimensionless BSA concentration during single ozonation and ozonation in the presence of AC_0 at pH 3 (a) and pH 7 (b); (C_0 = 1 mM, AC = 0.5 g/L, $C_{t\text{-}but}$ = 10 mM).

At pH 7 the decomposition of ozone into radical species is highly accelerated due to the high concentration of HO^-, which acts as an initiator of ozone decomposition. Therefore, a higher concentration of $HO^{\cdot}$ radicals is expected when compared to pH 3. In the presence of *tert*-butanol the degradation rate of BSA by single ozonation decreases significantly due to $HO^{\cdot}$ scavenging. In the same way, the catalytic

ozonation of BSA is also inhibited. However the results are still better in the presence of $AC_{0,}$ which suggests that another oxidation mechanism, such as surface reactions, also co-exists. The effect of the radical scavenger in the degradation of BSA is also evident when analysing the concentration of oxalic acid along time, as shown in Figure 6.5.

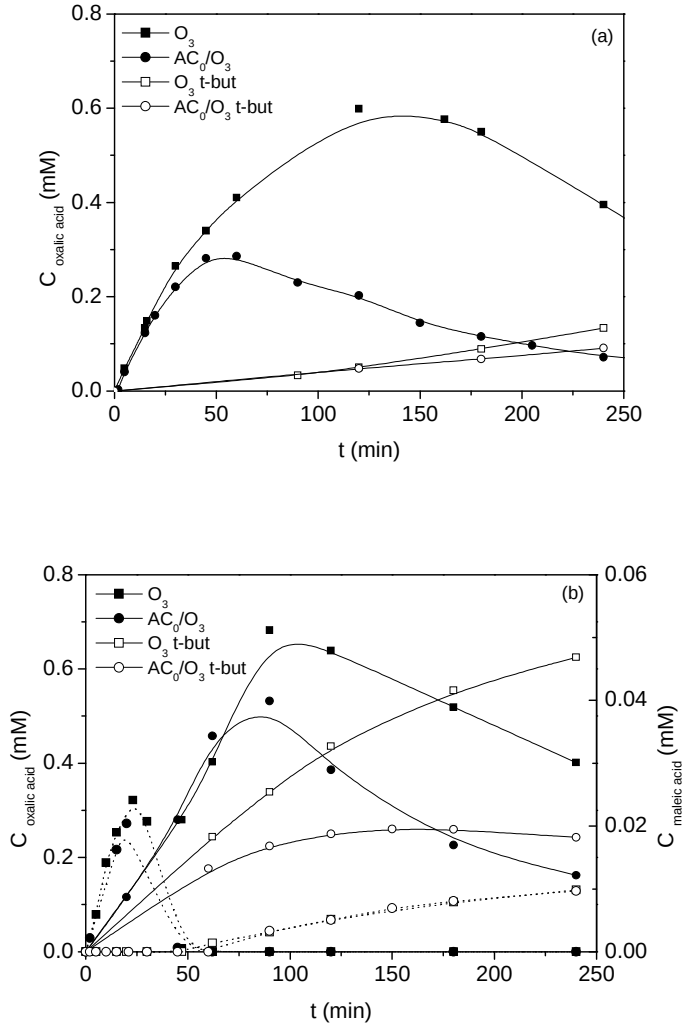


Figure 6.5. Influence of *tert*-butanol (C = 10 mM) on the concentrations of oxalic acid (solid lines) and maleic acid (dotted lines) resultant from the single ozonation and ozonation of BSA in the presence of AC_0 at pH 3 (a) and pH 7 (b).

As already said, oxalic acid is formed from the oxidation of BSA and is slowly mineralised during the reaction. At pH 3 (Figure 6.5a), low concentrations of oxalic acid are detected in solution, which is due to the fact that BSA degradation is highly inhibited by the presence of the radical scavenger. Nevertheless, at pH 7, when BSA is more effectively converted, higher concentrations of oxalic acid are detected along time. For single ozonation in the presence of *tert*-butanol, oxalic acid accumulates in solution at least during the first 4 h of reaction, due to its refractory character towards molecular ozone attack [20, 25]. On the contrary, in the presence of AC_0 and *tert*-butanol, it seems that oxalic acid concentration passes through a maximum, meaning that it is being removed. Even though the presence of *tert*-butanol inhibits the oxidation of oxalic acid via $HO^{\cdot}$ radicals in solution, this compound is believed to be oxidized on the surface of the activate carbon through a catalytic ozonation mechanism [20] (see chapter 5). At pH 7 also maleic acid is identified as one of the final oxidation products. As was shown in Figure 6.3, after 45 min of reaction, in the absence of the radical scavenger, no maleic acid was found in solution. On the opposite, in the presence of *tert*-butanol, maleic acid is slowly formed and accumulates in solution during the first 4 h of reaction.

6.3.2 Degradation of sulfanilic acid

The catalytic ozonation of sulfanilic acid was carried out at pH 3.3 (natural solution pH) and pH 7. As shown in Figure 6.6, sulfanilic acid is easily oxidized during single ozonation regardless of the solution pH. At acid pH, the addition of activated carbon to the ozonation process slightly improves its removal rate. This effect might be mostly due to the adsorption contribution than to a catalytic oxidation mechanism. At pH 7 no remarkable differences are observed between non catalytic and catalytic ozonation. In fact, at neutral pH this compound adsorbs less on both activated carbon samples, which corroborates the above explanation. Moreover, no major differences are observed between the results obtained by single ozonation at pH 3.3 and pH 7. This leads to the conclusion that the oxidation of SA is not strongly improved by a higher rate of ozone decomposition into oxygen-containing radicals, which are more reactive species.

On the other hand, an enhanced TOC removal is observed at pH 3.3 and pH 7 when activated carbon and ozone are used simultaneously. Both the pH effect and the catalytic effect produced by the presence of activated carbon are more visible when

analysing the concentrations of final oxidation products, such as small chain carboxylic acids. These compounds are usually refractory to molecular ozone attack, but react more effectively with $HO^{\cdot}$ radicals or through heterogeneous catalytic mechanisms.

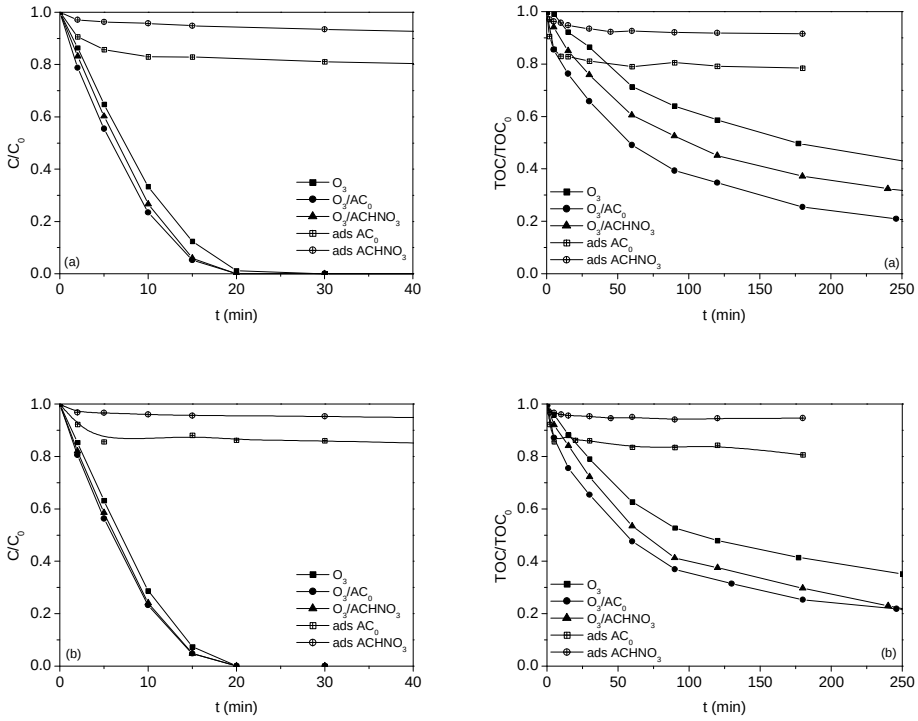


Figure 6.6. Dimensionless SA and TOC concentrations during adsorption, single ozonation and ozonation of SA in the presence of AC at pH 3.3 (a) and pH 7 (b); (C_0 = 1 mM, AC = 0.5 g/L).

Even though SA seems to be less refractory to oxidation than BSA, higher TOC removals are attained for solutions of the latter compound (cf. Figure 6.1 and Figure 6.6). This is related with the characteristics of the intermediates formed that are expected to be more refractory for SA. Actually, in the degradation of sulfanilic acid, oxalic acid and oxamic acid are formed and the latter is an extremely refractory carboxylic acid [20, 26].

Both carboxylic acids concentrations were followed, as these two compounds accumulate in solution and are responsible for the greatest fraction of TOC in solution at the end of the reaction. The results are depicted in Figure 6.7.

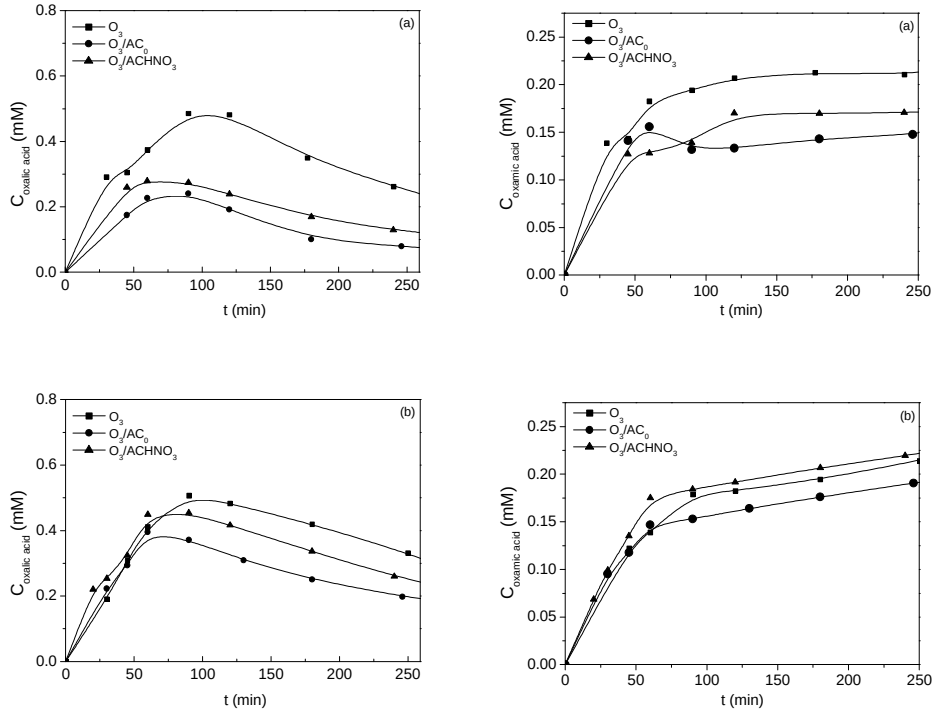


Figure 6.7. Evolution of oxalic acid and oxamic acid concentrations during catalytic and non-catalytic ozonation of SA at pH 3.3 (a) and pH 7 (b) (C_0 = 1 mM, AC = 0.5 g/L).

At pH 3.3 both acids are refractory to single ozonation but their mineralisation rate is greatly enhanced in the presence of activated carbon, mainly in this case of oxalic acid. In the presence of activated carbon the corresponding concentrations are always lower, which indicates a faster removal rate, especially with sample AC_0. In a previous work [20] (see chapter 5), oxamic acid was found to be highly refractory to single ozonation. The ozonation catalysed by activated carbon enhanced the mineralisation of oxamic acid at low pH. However, at neutral and basic pH no significant mineralisation was accomplished. As expected, during the oxidation of sulfanilic acid at pH 3.3, the presence of activated carbon enabled the decrease of oxamic acid concentration in solution. On the other hand, at pH 7 no major

differences in oxamic acid concentrations are observed when comparing catalytic with non-catalytic ozonation, which is in agreement with previous results [20] (see chapter 5).

The mineralisation of SA is accompanied by the conversion of its initial nitrogen and sulphur moieties into inorganic ions. Both ammonium NH_4^+ and nitrate NO_3^- ions were detected during the ozonation of SA. Figure 6.8 depicts the evolution of the concentrations of those inorganic ions during single ozonation and ozonation in the presence of activated carbon at pH 3.3 and pH 7.

During the first 30 min of reaction there is a fast accumulation of NH_4^+, probably due to the quick conversion of N-containing products in the early stage of the ozonation process, and it is coincident with the disappearance of SA. For longer reaction times, the NH_4^+ concentration does not change, pointing out that the decomposition of refractory intermediates produced during the oxidation of SA does not lead to the release of NH_4^+. During the oxidation process NO_3^- is formed and accumulates in solution. According to the experimental results, the formation of NH_4^+ is favoured at acid pH and production of NO_3^- at pH 7. This observation suggests different reaction mechanisms depending on the solution pH. However, the lack of knowledge of great part of the reaction intermediates prevents a more detailed discussion on this matter.

Regardless of the solution pH, the concentrations of NO_3^- were always lower whenever the ozonation of SA was carried out in the presence of activated carbon. This might be due, to the formation of different N-containing intermediates in the presence or absence of activated carbon and to the adsorption of some of those intermediates. Moreover, the ozonation of such compounds in the presence of activated carbon may follow a route that does not lead to the formation of NO_3^-, as was reported for the catalytic ozonation of oxamic acid [20] (see chapter 5).

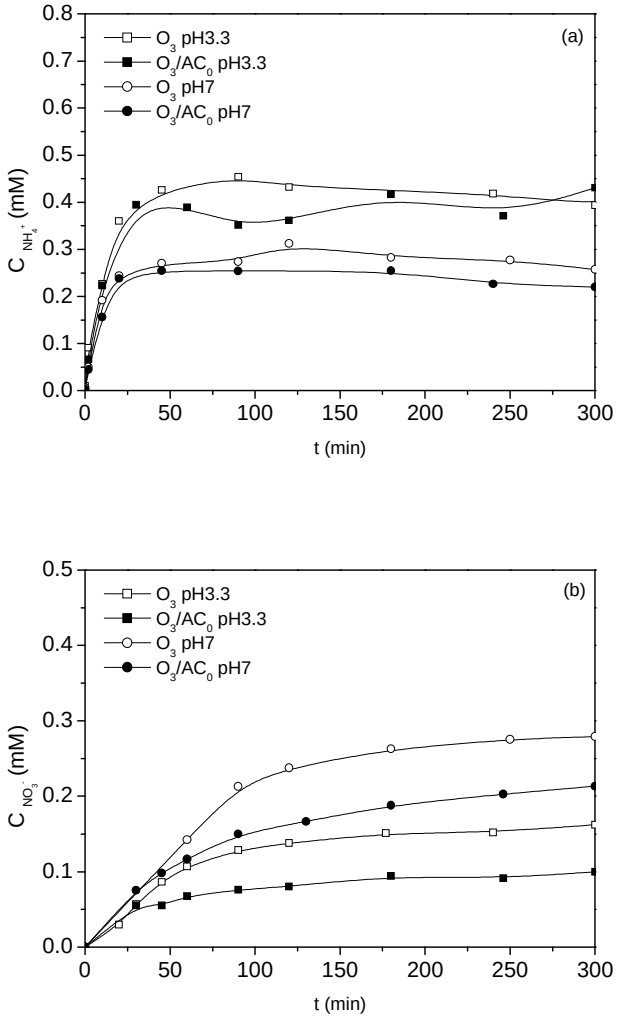


Figure 6.8. Evolution of NH_4^+ (a) and NO_3^- (b) concentrations during catalytic and non-catalytic ozonation of SA at pH 3.3 and pH 7 (C_0 = 1 mM, AC = 0.5 g/L).

As previously shown (Figure 6.6), the elimination of SA by single ozonation is not severely influenced by the solution pH in the range studied, i.e., similar removal rates are observed at acid and neutral pH. This might mean that the oxidation mechanism of SA is not highly dependent on the concentration of $HO^{\cdot}$ radicals in solution. In fact it was observed that, oppositely to what happened with BSA, the presence of a radical scavenger did no inhibit the decay of SA concentration. In

fact, the elimination of SA at pH natural seems to be slightly favoured by the presence of *tert*-butanol, while at pH 7 no significant differences were observed, as shown in Figure 6.9. The positive effect observed at pH 3.3 might be ascribed to a stabilization of the dissolved ozone. In the presence of *tert*-butanol, $HO^{\bullet}$ species (which participate in the ozone decomposition chain-reaction mechanism) are consumed, slowing down the decomposition of ozone.

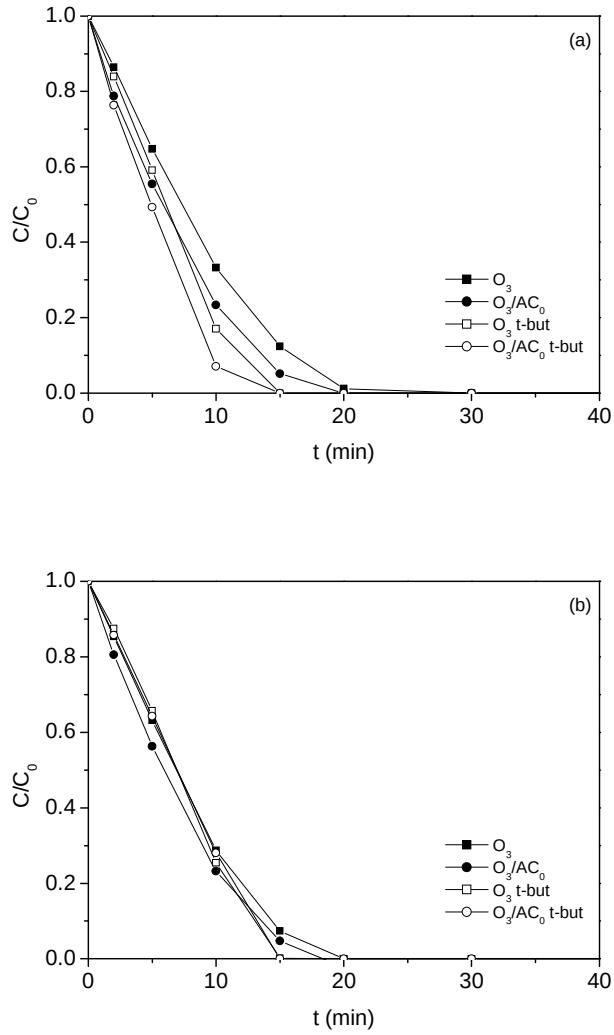


Figure 6.9. Influence of *tert*-butanol on the dimensionless SA concentration during single ozonation and ozonation in the presence of AC_0 at pH 3.3 (a) and pH 7 (b); (C_0 = 1 mM, AC = 0.5 g/L, $C_{t\text{-}but}$ = 10 mM).

The experimental results suggest that sulfanilic acid molecule is more easily oxidized than the BSA molecule. The presence of the strong activating group -NH_2, activates the aromatic ring by increasing its electron density through a resonance donating effect. The resonance allows electron density to be positioned at the *ortho*- and *para*- positions. Hence these sites are more nucleophilic, and the system tends to react with electrophiles at these sites. Therefore, sulfanilic acid is susceptible of being attacked by molecular ozone preferentially at those sites.

Similarly to what was described for the BSA, the effect of the radical scavenger is visible when analysing the evolution of the concentrations of both carboxylic acids followed during the ozonation of sulfanilic acid (Figure 6.10).

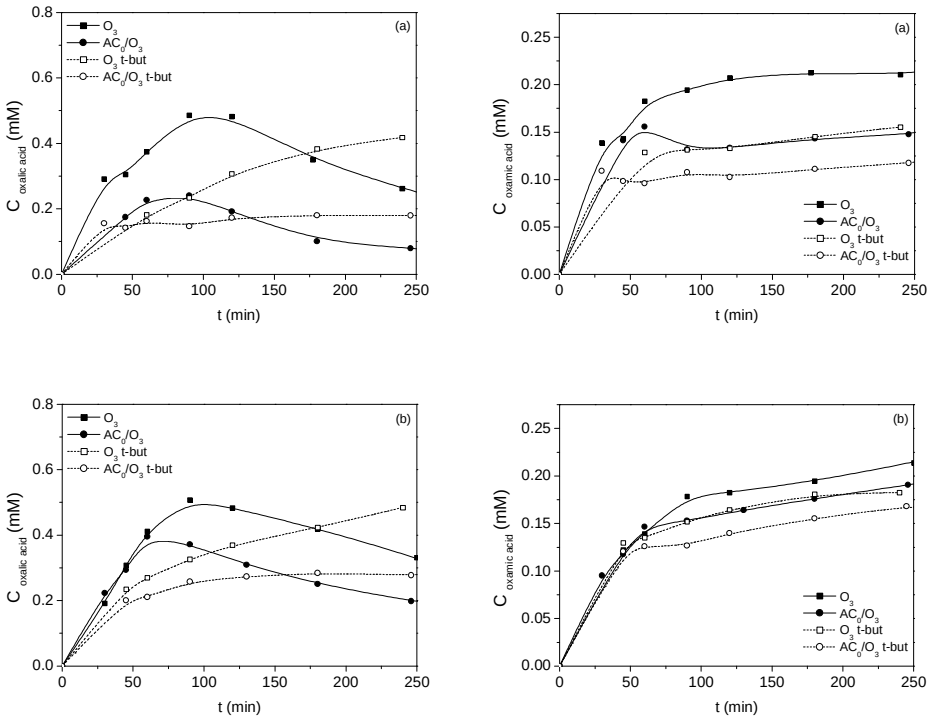


Figure 6.10. Influence of *tert*-butanol (C = 10 mM) on the concentrations of oxalic and oxamic acids resultant from single ozonation and ozonation of SA in the presence of AC_0 at pH 3.3 (a) and pH 7 (b).

During single ozonation of SA in the presence of the radical scavenger, oxalic acid accumulates in solution during the first 4 hours, while in the presence of activated

carbon it seems that oxalic acid is simultaneously being formed and removed, as the concentration is approximately constant after an initial accumulation period (lower at pH 3.3). According to the previous reasoning, even though the presence of *tert*-butanol inhibits the oxidation of oxalic acid via $HO^{\cdot}$ radicals in solution, this compound is believed to be oxidized on the surface of the activate carbon through a catalytic ozonation mechanism [20] (see chapter 5). Though it was not possible to identify all the intermediaries of the reaction, the qualitative analysis of the HPLC chromatograms shows that, in the presence of *tert*-butanol, there is a higher amount of reaction products comparatively to the experiments in the absence of *tert*-butanol. Nevertheless, whenever activated carbon is present, a decrease in the concentration of those products is observed, which means that other mechanism, besides oxidation via $HO^{\cdot}$ in solution also occurs.

In the presence of *tert*-butanol the concentration levels of both oxalic and oxamic acids are generally lower than those detected without *tert*-butanol. In fact, the presence of *tert*-butanol does not inhibit the oxidation of SA but strongly inhibits further mineralisation of the oxidation intermediates. Considering that both oxalic and oxamic acid are final oxidation products, it is possible that their concentrations are lower, as other by-products are also present when the reaction is carried out in the presence of a radical scavenger.

6.3.3 Considerations about the reaction mechanism

The removal of both BSA and SA, as well as the respective oxidation by-products, via ozonation in the presence of activated carbon is a result of a complex combination of homogeneous and heterogeneous reactions. Both direct and indirect ozone reactions occur in the liquid phase. Additionally, reactions between adsorbed species and oxygenated radicals formed on the surface of the activated carbon are assumed to occur.

Regarding the non-catalytic decomposition of ozone in aqueous solution, it is established that it is initiated by the presence of HO^{-} ions; so pH plays a major role in this process:

$$O_3 \xrightarrow{HO^-} HO^{\bullet} \qquad (6.1)$$

Several authors have reported that activated carbon accelerates the decomposition of ozone [12-16]. Both textural and surface chemical properties influence that

decomposition, but doubts on the mechanism still remain. According to the literature, two possible pathways can explain the decomposition of O_3 in the presence of activated carbon. The first one assumes that activated carbon acts as an initiator of the decomposition of ozone, eventually through the formation of H_2O_2 [10], yielding free radical species, such as $HO^{\cdot}$, in solution [15]:

$$O_3 \xrightarrow{AC} HO^{\bullet} \tag{6.2}$$

Another possibility is the adsorption and reaction of ozone molecules on the surface of the activated carbon, yielding surface free radicals [12]:

$$AC + O_3 \rightarrow AC - O \tag{6.3}$$

where AC-O stands for any oxygen-containing active species on the surface of the activated carbon, which can react with adsorbed organic species [27].

Aromatic compounds (Ar) that are substituted by electron donor groups, such as -OH and $-NH_2$, have a high electronic density in *ortho*- and *para*- positions. Consequently, such aromatic compounds react actively in those positions with ozone by electrophilic attack. This results in the formation of several intermediates that are further transformed into saturated compounds (*I*), which cannot be mineralised by direct ozone attack. Additionally, $HO^{\cdot}$ radicals can also contribute to the oxidation of the aromatic compounds, as was shown for BSA, which seem to be refractory to direct ozone attack. The mineralisation of the oxidation intermediates into CO_2 and inorganic ions (e.g. NO_3^-, NH_4^+, SO_4^{2-}), represented by *P*, occurs both in the liquid phase through $HO^{\cdot}$ radical attack, or on the surface of the activated carbon. Steps (6.4) to (6.8) schematically represent the proposed pathways.

$$Ar + O_3 \rightarrow I \tag{6.4}$$

$$Ar + HO^{\bullet} \rightarrow I \tag{6.5}$$

$$I + HO^{\bullet} \rightarrow P \tag{6.6}$$

$$AC + I \rightarrow AC - I \tag{6.7}$$

$$AC - I + AC - O \rightarrow P \tag{6.8}$$

Even though there is no experimental evidence, it is necessary to consider that adsorbed reactants might also react with dissolved ozone, or hydroxyl radicals from the aqueous phase, according to Beltrán et al. [28], who made similar assumptions regarding the ozonation of pyruvic acid catalysed by activated carbon.

$$AC + Ar \rightarrow AC - Ar \quad (6.9)$$

$$AC - Ar + O_3 \, or \, HO^{\bullet} \rightarrow I \quad (6.10)$$

It was shown that the presence of the radical scavenger (*tert*-butanol) induced different results depending on the aromatic compound studied. It inhibited the conversion of BSA, but no significant effect was observed for SA. However, in both cases the removal of oxidation by-products was influenced by the radical scavenger, which suggests the formation and reaction of $HO^{\cdot}$ radicals. This supplies experimental evidence for the occurrence of steps (6.5) and (6.6).

6.4 Conclusions

In the present work, the mineralisation of two selected model compounds of sulfonated aromatic by-products found in industrial effluents was studied. The ozonation of benzenesulfonic acid (BSA) and sulfanilic acid (SA) leads to complete conversion of both compounds after a short reaction period. As a result, the removal of these non-biodegradable compounds from aqueous solutions can be accomplished by chemical oxidation.

The presence of activated carbon during ozonation of BSA and SA increases their rate of degradation and mostly enhances the reduction of TOC. The use of a basic activated carbon is advantageous for this process. On one hand, adsorption of organic compounds is favoured and, additionally, basic activated carbons are believed to have an enhanced ability to catalyse the decomposition of ozone in aqueous phase into more reactive radical species, both on the liquid phase and on activated carbon surface.

Even though BSA seems to be more refractory to oxidation than SA, higher TOC removals are attained with solutions of the former compound. This is related with the characteristics of the intermediates formed, which seem to be more refractory in the case o sulfanilic acid. In fact, one of the final ozonation products is oxamic acid, which is a highly refractory carboxylic acid.

The presence of a radical scavenger during single ozonation evidenced the participation of $HO^{\cdot}$ radicals in the oxidation mechanism, especially in the degradation of BSA and in the mineralisation of the oxidation by-products. In the combined treatment, the effects of radical scavengers were reduced due to the

presence of activated carbon, which suggests that carbon surface plays a role in the reaction mechanism. Thus, activated carbon provides a surface where reactions between organic species and ozone or free radicals occur, i.e., acts directly as a catalyst.

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Part IV

Ozonation of Model Organic Compounds Catalysed by Metal Oxide Based Catalysts

Supported and unsupported oxides of transition metals are frequently studied ozonation catalysts. Among them, cobalt and manganese oxides have proven to be efficient ozonation catalysts. Nevertheless, metal leaching and low stability are sometimes associated to the use of such materials in ozonation reactions. Due to the importance of catalytic ozonation as a promising technology for the elimination of recalcitrant compounds from water and wastewater, the continuous search for more efficient catalysts is of great importance.

In this part of the work, a screening test of several metal oxides such as manganese, cobalt and cerium, as well as binary mixtures of these metal oxides, was carried out. The performance of those materials was evaluated in the mineralisation of aniline and sulfanilic acid. Simultaneously, metal oxides supported on activated carbon were also prepared and tested in the ozonation of aniline, sulfanilic acid and dye CI acid blue 113 (chapter 7).

Among the metal oxides tested, cerium oxide was shown to be an effective and stable ozonation catalyst. Contrary to the manganese and cobalt oxides, no much information is available in the literature regarding the use of cerium oxide as ozonation catalysts in the aqueous phase. Considering the former reasons, cerium oxide was selected for further research.

In order to combine the properties of activated carbon and search for possible synergetic effects, a cerium oxide-activated carbon composite was prepared and tested in the ozonation of organic compounds. Using the same approach of the previous chapters, both cerium oxide and composite were tested first in the ozonation of carboxylic acids (chapter 8), followed by the three previously selected aromatic compounds (chapter 9). Some considerations were presented regarding the steps involved in the reaction mechanism.

7 Metal Oxides as Catalysts for the Ozonation of Selected Organic Compounds[1,2]

Several metal oxides, as well as metal oxides supported on activated carbon, were assessed as ozonation catalysts for the removal of selected organic compounds. Two transition metals (Mn, Co) and one rare earth element (Ce) were chosen for the preparation of the two series of catalysts. These materials were used in the ozonation of two aromatic compounds (aniline and sulfanilic acid) and one textile azo dye (CI acid blue 113). The results were compared with those obtained with non-catalytic ozonation. All the tested materials were found to be effective ozonation catalysts. Among the metal oxides, those containing mixtures of cerium and manganese or cerium and cobalt enabled higher mineralisation rates. Regarding the metal oxides supported on activated carbon, cerium oxide was the most active for the degradation of the studied compounds.

7.1 Introduction

Aromatic amines and sulfonated aromatic compounds are common pollutants present in several industrial effluents, as is the case of textile processing industry wastewater. Such compounds may arise from the biodegradation of dyes, especially from those containing azo chromophores ($-N=N-$). Generally, these pollutants are not susceptible to anaerobic or aerobic biodegradation, and their elimination cannot be accomplished by conventional biological treatments [1, 2]. Chemical oxidation processes may be used as an alternative and/or as a complement to biological treatments, in order to accomplish a faster and higher mineralisation of those compounds. Among the available oxidative destructive treatments, ozonation is becoming increasingly important as a final (post)treatment technology to improve

[1] Based on PCC Faria, DCM Monteiro, JJM Órfão, MFR Pereira, *submitted* (2008).

[2] Additional data presented in Appendix E.

the removal of colour and the elimination of persistent pollutants present in bio-treated effluents [3]. Ozone is capable of oxidising a vast range of organic compounds, especially those containing unsaturated bonds or aromatic moieties, but, typically, single ozonation rarely leads to total mineralisation. Instead, saturated compounds such as aldehydes and small chain carboxylic acids are formed from the partial oxidation of the initial organic pollutants present in solution.

Several studies have shown that catalytic ozonation is a promising technique to destroy more recalcitrant pollutants [4]. Generally, catalytic ozonation is focused on the activation of ozone by numerous metal ions (Fe, Mn, Ni, Co, Zn, Ag, Cr) in solution or by heterogeneous catalysts with metals under various forms (salt of reduced metal, solid oxide, supported metal). Heterogeneous catalytic ozonation aims to enhance the removal of more refractory compounds through the transformation of ozone into more reactive species and/or through adsorption and reaction of the pollutants on the surface of the catalyst [5].

The most common catalysts proposed for the process of heterogeneous catalytic ozonation are metal oxides such as MnO_2, TiO_2, Al_2O_3, ZnO and supported metal oxides (TiO_2/Al_2O_3, Fe_2O_3/Al_2O_3, Co_3O_4/Al_2O_3, MnO_2/TiO_2). Transition and noble metals supported on several oxides (Cu-Al_2O_3, Cu-TiO_2, Co-Al_2O_3, Ru-CeO_2,) have also been investigated in ozonation reactions [4, 5]. Despite the number of papers published on this subject, there is still opportunity for the development and evaluation of alternative ozonation catalysts. Cerium-based catalysts have been extensively studied for the application in several processes, including wet air oxidation reactions [6-8]. However, only a few studies have reported the use of cerium containing catalysts for the ozonation of organic compounds [9, 10]. Mixed or composite oxides of several metals such as Co/Bi, Co/Ce or Mn/Ce have been reported as effective catalysts in the wet catalytic oxidation of different organic and inorganic compounds [7, 11], but no such materials have been tested in aqueous ozonation reactions.

In the present work, the preparation of a series of manganese, cobalt and cerium oxides, as well as composite oxides of manganese-cerium or cobalt-cerium was carried out, with the aim of evaluating their performance as ozonation catalysts for the mineralisation of organic pollutants in aqueous solution. For that purpose, aniline, sulfanilic acid, and the azo dye CI acid blue 113 were selected as model compounds, and TOC analysis was chosen as the main analytical technique for the

evaluation of the catalysts efficiency. In previous work [12, 13] (see chapter 5 and 6), activated carbon was found to enhance the ozonation of several aromatic and carboxylic acids. Additionally, due to its textural and surface chemical features, activated carbon is widely used as a catalyst support [14]. Therefore, Mn, Co and Ce oxides supported on activated carbon were also assessed in the ozonation of the selected compounds and the results were compared with those obtained with the support.

7.2 Experimental

7.2.1 Materials

Three organic molecules were selected for this study: a textile dye (CI acid blue 113) with known molecular structure, and two aromatic compounds, aniline and sulfanilic acid, which are often produced from the biodegradation of azo compounds.

Two different sets of catalysts were prepared. The first one is comprised of single and composite oxides prepared by precipitation [7] from the corresponding salt aqueous solutions ($Ce(NO_3)_3.6H_2O$; $Co(NO_3)_2.6H_2O$, $C_4H_6MnO_4.4H_2O$). In each batch, 200 mL of a sodium hydroxide 3 M solution was added drop wise to a metal salt solution (ca. 15 g / 100 mL H_2O) under continuous stirring. The resultant precipitates were thoroughly washed with distilled water, dried at 100 ºC for 24 h and calcinated in air (50 cm^3 min^{-1}, measured at room T and P) at 450 ºC for 3 h. The catalysts were sieved before use and a particle size of 100-300 μm was selected for the kinetic experiments. The composite oxides were prepared by co-precipitation from a mixed aqueous solution of the corresponding salts, with equimolar fractions of the metals. The catalysts were labelled as follows: Mn-O, Co-O, Ce-O, Ce-Mn-O, Ce-Co-O.

The second set of catalysts consists of metal oxides supported on activated carbon. A commercial activated carbon, NORIT GAC 1240 PLUS (sample AC), was used as support for the preparation of catalysts. It was impregnated by the incipient wetness method from the corresponding salt solutions in order to achieve 5% (w/w) of each metal: Mn, Co or Ce. After drying at 100 ºC for 24 h, the catalysts were thermally treated in N_2 (50 cm^3 min^{-1}, measured at room T and P) at 400 ºC for 1 h. The materials were labelled as follows: AC_5%Mn, AC_5%Co, AC_5%Ce.

The textural characterization of the materials was based on the corresponding N_2 equilibrium adsorption isotherms, determined at 77 K with a Coulter Omnisorp 100 CX apparatus. As reference, the BET surface areas (S_{BET}) of the samples were calculated. X-ray diffraction (XRD) spectra were recorded on a Philips X'Pert MPD diffractometer (Cu Kα = 0.15406 nm). The morphology and the semi-quantitative elemental composition of the composite oxides were analysed by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) on a JEOL JSM 35C/Noran Voyager system.

7.2.2 Experimental set-up and analytical methods

All the experiments were carried out in a slurry lab-scale reactor (ca. 1 L) with magnetic stirring. In each experiment the reactor was filled with 700 mL of the selected compound solution, at the desired concentration (1mM for aniline and sulfanilic acid; 100 mg/L for CI acid blue 113). In the catalytic experiments, 350 mg of catalyst (particle size = 100 - 300 μm) were introduced in the reactor. The reactions were carried out at 25 ºC and at the natural pH of the solutions. Ozone was produced from pure oxygen in a BMT 802X ozone generator. The experiments were performed at constant gas flow (150 cm^3 min^{-1}, measured at room T and P) and constant inlet ozone concentration (50 g Nm^{-3}). The concentration of ozone in the gaseous phase was monitored with a BMT 964 ozone analyzer.

The concentrations of aniline and sulfanilic acid were followed by HPLC analysis using a Hitachi Elite Lachrom HPLC equipped with a diode array detector. The stationary phase was a YMC Hydrosphere C18 column (250 mm x 4.6 mm) working at room temperature, under isocratic elution with a mixture of water, acetonitrile and *o*-phosphoric acid at pH 2. The concentration of dye was followed by UV-Vis spectrophotometry at the maximum absorption wavelength (566 nm), previously determined. The degree of mineralisation was followed by TOC analysis in a Shimadzu TOC-5000A Analyzer.

7.3 Results and discussion

7.3.1 Characterization of the catalysts

Figure 7.1 shows the X-ray diffraction patterns of all the prepared oxides and the corresponding main oxide phases identified in each sample are listed in Table 7.1. The X-ray analysis of the composite oxides did not suggest the presence of any other compounds besides the single oxides. In sample Ce-Mn-O the dominant diffraction peaks are those characteristic of cerianite (CeO_2). This may be due to the formation of Ce-Mn oxide with cerianite structure or to the occurrence of amorphous manganese oxides [6]. The XRD spectrum of sample Ce-Co-O reveals the presence of Co_3O_4 besides the characteristics peaks of CeO_2. Regarding the metal oxides supported on activated carbon, no crystalline phases were identified on the XRD diffractograms.

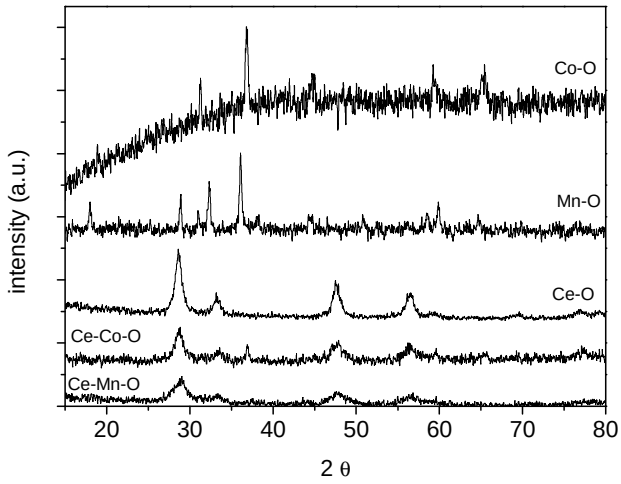


Figure 7.1 X-ray diffractograms of the single and composite metal oxides.

Table 7.1 Characterization of the metal oxides.

	Mn-O	Co-O	Ce-O	Ce-Mn-O	Ce-Co-O
S_{BET} (m^2/g)	26	29	72	114	87
Oxide phases[1]	Mn_3O_4	Co_3O_4	CeO_2	CeO_2	CeO_2 Co_3O_4

[1] identified from XRD patterns.

Samples Ce-Mn-O and Ce-Co-O were analysed by SEM at different magnifications. SEM and EDS analyses of sample Ce-Mn-O revealed the presence of distinct layers enriched in manganese or cerium, as can be observed in zones Z1 and Z2 depicted in Figure 7.2.

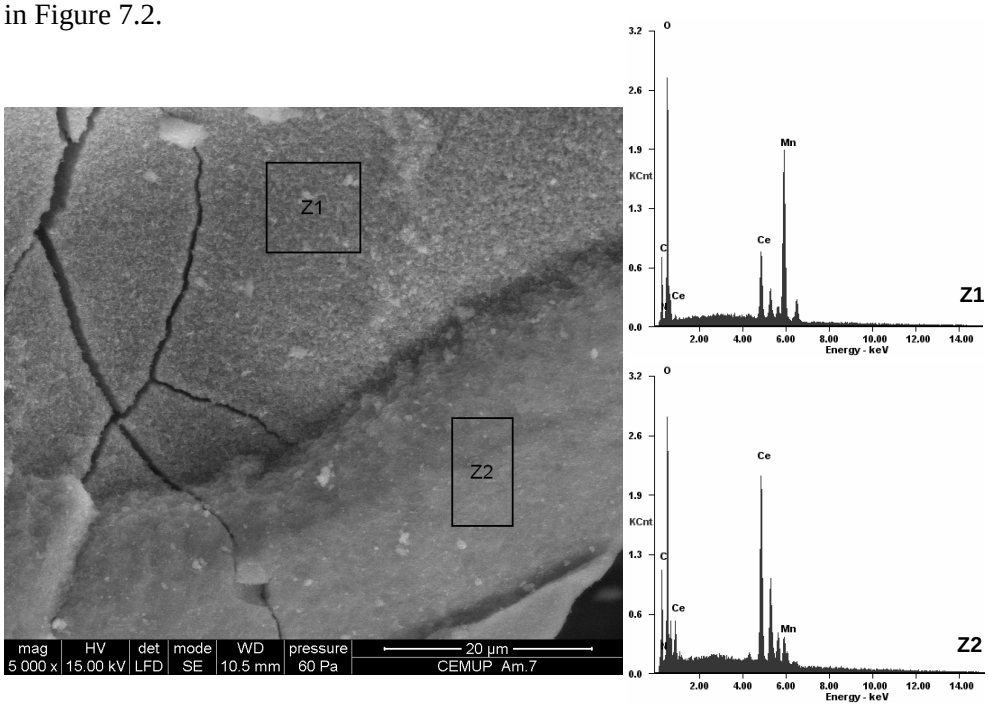
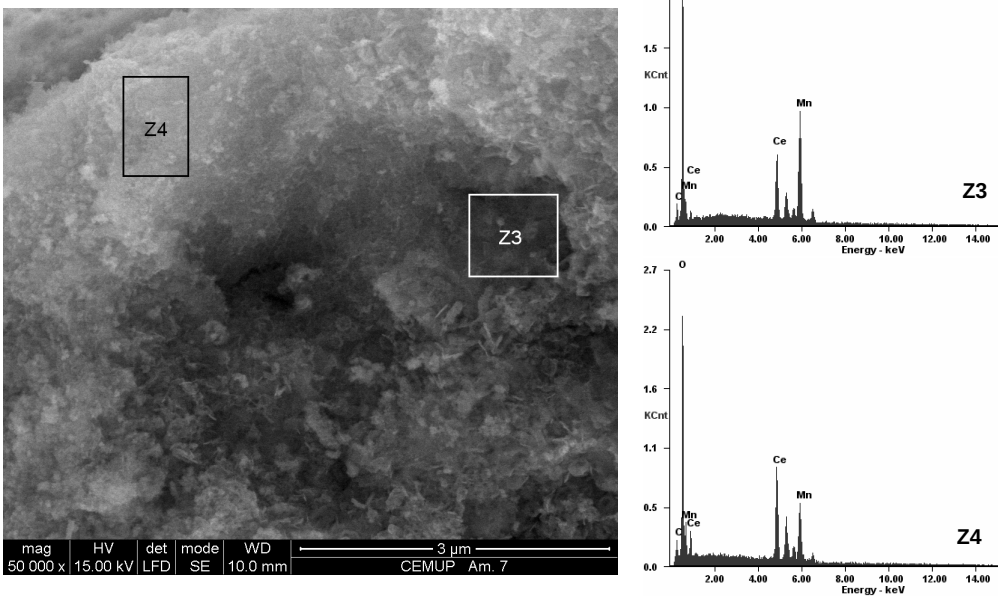


Figure 7.2 SEM image of sample Ce-Mn-O and EDS analyses of zones Z1 and Z2.

(a)



(b)

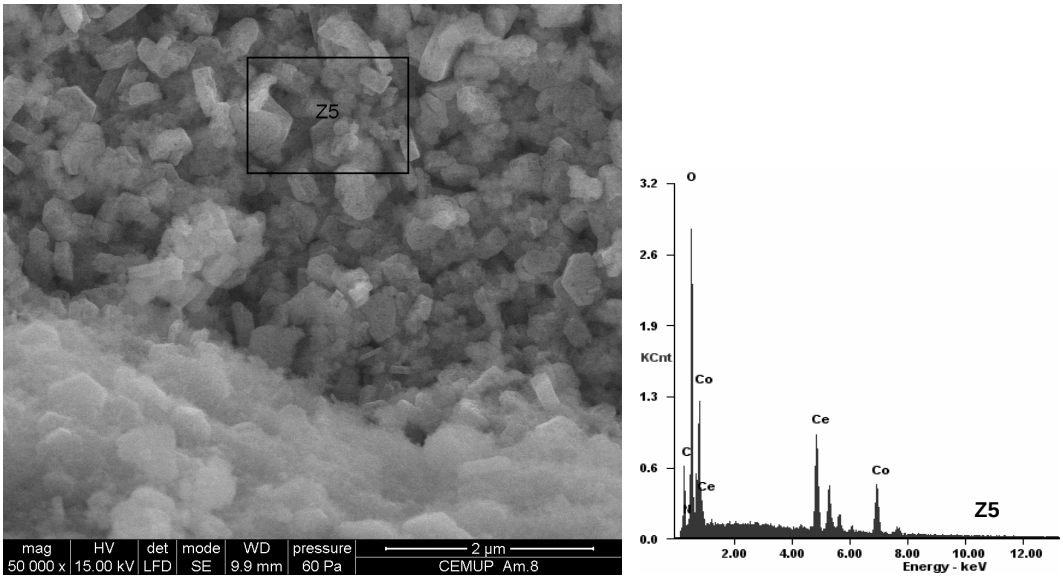


Figure 7.3 SEM images of samples (a) Ce-Mn-O and (b) Ce-Co-O and EDS analyses of zones Z3, Z4 and Z5.

Images with higher magnification (Figure 7.3a) show that there are zones where the distribution of cerium and manganese is more homogeneous. Nevertheless, those areas are either richer in Mn (Z3) or Ce (Z4). Figure 7.3b shows that the morphology of sample Ce-Co-O is quite different from that sample Ce-Mn-O. Additionally, EDS analysis revealed that the particles of that composite oxide have a homogeneous distribution of cerium and cobalt and no major composition differences were detected within the catalyst particles.

The BET surface areas of the metal oxides are listed in Table 7.1. Among the single metal oxides, cerium oxide is that with the highest surface area. The preparation of composite metal oxides results in materials with significantly higher surface areas, which is in agreement with results reported in the literature [7].

The selected activated carbon has a BET surface area of 909 m^2/g and the complete characterization of this material is reported elsewhere [15] (see chapter 2). The supported catalysts have a slightly lower specific surface area comparatively to the commercial activated carbon.

7.3.2 Ozonation catalysed by metal oxides

Both the single and the composite metal oxides prepared by precipitation were tested as catalysts in the ozonation of aqueous solutions of aniline and sulfanilic acid. The results obtained in terms of TOC removal are presented in Figure 7.4, along with the results obtained by non-catalytic ozonation, for comparative purposes.

The conversion of aniline and sulfanilic acid can be accomplished by single ozonation in a relatively short reaction period, which is also supported by the results obtained previously [13, 16] (see chapters 4 and 6). Ozone is an extremely powerful oxidant capable of reacting with a vast range of compounds, and it attacks selectively aromatic moieties and unsaturated bonds.

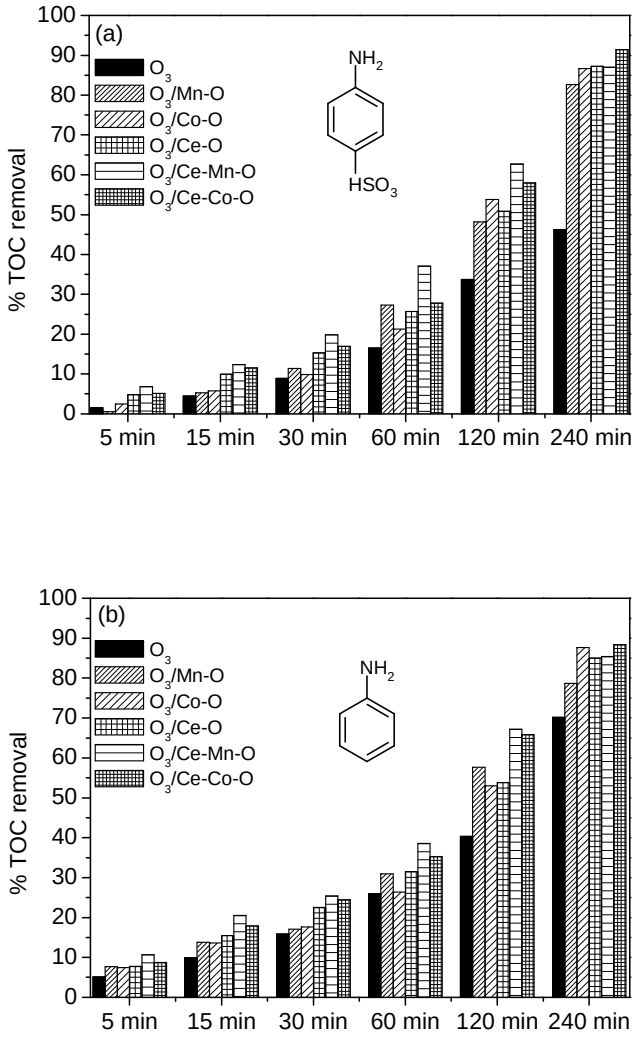


Figure 7.4 Evolution of TOC removal during single ozonation and metal oxides catalytic ozonation of (a) sulfanilic acid (pH_i = 3) and (b) aniline (pH_i = 6) (C_0 = 1 mM, catalyst = 0.5 g/L).

Aromatic compounds possessing electron donor groups, such as -NH_2, have a high electronic density in *ortho*- and *para*- positions and react actively with ozone by electrophilic attack. This results in the formation of several intermediates that are further transformed into saturated compounds, such as small chain carboxylic acids, which are not mineralised by direct ozone attack. Therefore, the degree of

mineralisation attained in the single ozonation of the selected compounds is not always satisfactory. Under the experimental conditions used in this work, the TOC removal achieved by single ozonation for the solutions of aniline and sulfanilic acid was ca. 70% and 46%, respectively, after approximately 4 h of reaction. Apparently, aniline solutions are less refractory to ozonation than those of sulfanilic acid. However, the pH effect cannot be discarded. The ozonation of aniline was carried out at a pH around 6, while sulfanilic acid was oxidized at pH 3. It is known that ozone self decomposition in aqueous phase originates $HO^{\cdot}$ free radicals that are highly reactive and responsible for the mineralisation of a vast number of organic compounds. At higher pH, ozone self-decomposition into highly reactive radical species is accelerated, therefore leading to higher mineralisation rates.

The presence of the metal oxides clearly enhanced the mineralisation of the studied solutions. According to the experimental data depicted in Figure 7.4, all the catalysts tested presented a significant catalytic effect. Among the single metal oxides, no major differences were observed in terms of their efficiency for TOC removal. From the early stages of the reaction, both composite oxides, Ce-Mn-O and Ce-Co-O, were visibly active for the mineralisation of sulfanilic acid and aniline. In general, those materials presented slightly better results than the individual oxides. Such result may be attributed to the higher specific surface areas of the mixed oxides, comparatively to the single ones, especially in the case of Ce-Mn-O (see Table 7.1).

In all cases, the catalytic effect was more distinct in the ozonation of sulfanilic acid, comparatively to aniline, which is related to the fact that, under the experimental conditions used, single ozonation of sulfanilic acid leads to a lower mineralisation extent. Nevertheless, when comparing the TOC removal of both compounds obtained with the different catalytic systems, after 4 h, mineralisation degrees lie between 80 and 90%, approximately. The remaining TOC is mostly due to the formation of by-products of refractory nature, as is the case of oxamic acid, which is in agreement with the literature [12, 13].

The ozonation of organic compounds involves a number of complex reactions and many mechanistic approaches have been presented in the literature. It is widely accepted that ozone reacts in aqueous solution with various organic and inorganic compounds, either by direct reaction of molecular ozone or through a radical type reaction involving $HO^{\cdot}$ radicals resultant from the decomposition of ozone in water. In heterogeneous catalytic ozonation, it is generally assumed that both surface and

liquid bulk reactions can occur, involving molecular ozone, $HO^{\cdot}$ radicals and surface oxygenated radical species [5].

Concerning cobalt oxide-based catalysts, several authors have reported their efficiency in the mineralisation of organic pollutants. Álvarez et al. [17] investigated different Co active phases deposited on the γ-Al_2O_3 surface (CoO, $CoAl_2O_4$, Co_3O_4) and reported that the sample containing Co_3O_4 as the main Co phase provided the most promising results on the ozonation of pyruvic acid. Recently, Hu et al. [18] investigated the ozonation of an herbicide over cobalt oxide supported on mesoporous zirconia, which were found to be active for the degradation of that compound. Cobalt oxide is mainly present as Co_3O_4, and the enhanced mineralisation of that compound achieved by catalytic ozonation was manly due to the presence of $HO^{\cdot}$, generated from the catalytic decomposition of ozone. The high dispersion of Co oxide on the support and the multivalence oxidation states of cobalt (Co (II) and Co (III)) was suggested to be responsible for the catalytic reactivity of the catalyst. Even though the discussion of the reaction mechanism involved in the catalysed ozonation of aniline and sulfanilic acid was not the main focus of this chapter, it is probable that the activity of cobalt oxide may be related with the existence of multivalence oxidation states on the metal oxides surface, as suggested by Hu et al. [18].

Manganese oxides, especially MnO_2 are frequently cited in the literature as being highly effective in catalytic ozonation reactions. The activity of such materials has been evaluated in the ozonation of several organic compounds such as atrazine, oxalic acid, phenolic compounds, sulfosalicylic acid and propionic acid [5]. However, divergences exist on the proposed reaction mechanism present in the literature. While some authors suggest the formation of surface complexes easily oxidized by ozone [19], others attribute the catalytic effect to the generation of $HO^{\cdot}$ radicals from the decomposition of ozone, initiated on the surface of the catalyst [20]. In this work, Mn_3O_4 was the main crystalline phase detected by XRD (Table 7.1) and was found to be an active ozonation catalyst for the mineralisation of the selected compounds. As well as Co_3O_4, manganese oxide (Mn_3O_4) is also an intrinsic semi-conductor, as manganese presents both +2 and +3 valences. Thus, according to what has been proposed for the cobalt oxides, it could be assumed that the presence of such species has a promoting effect in ozonation reactions.

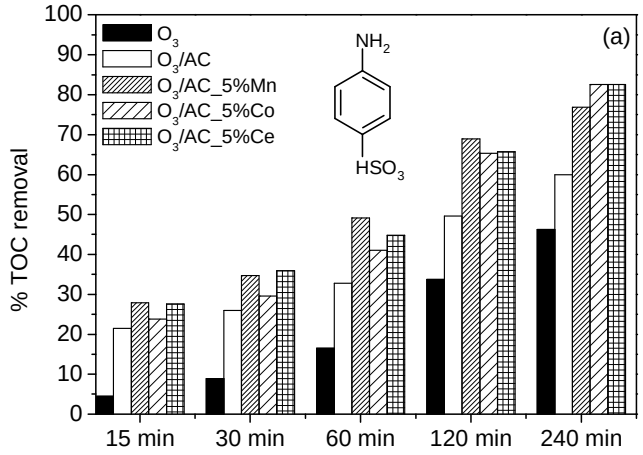
Regarding cerium containing catalysts, only a few studies have reported their use for the ozonation of organic compounds [9, 10]. Matheswaran et al. [10] found a

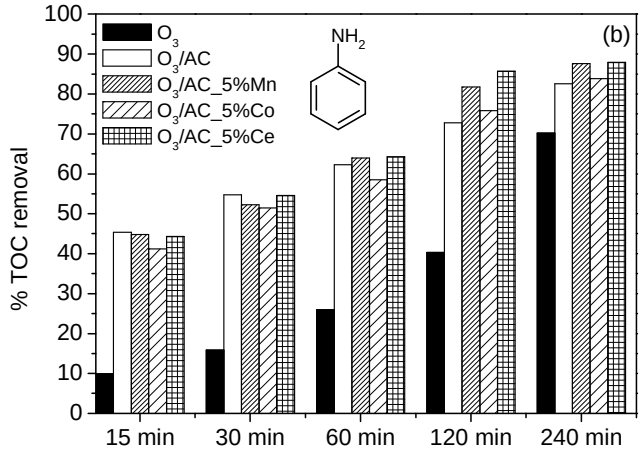
significant synergic effect between the cerium redox pair (Ce^{3+}/Ce^{4+}) and ozone towards phenol mineralisation. Leitner et al. [9] reported the use of CeO_2 as ruthenium support for the oxidation of succinic acid in aqueous solution. In that work, the support was shown to have a slight catalytic activity in the removal of this carboxylic acid, but no further considerations were made on the catalytic effect of cerium oxide. In the present work, both single and composite metal oxides containing cerium were found to be potential catalysts for the ozonation of aniline and sulfanilic acid. During the eighties, Imamura et al. [7] first found that composite oxides of cerium-cobalt (CeO_2-Co_3O_4), and cerium–manganese (CeO_2-Mn_2O_3) were effective and stable catalysts in the wet oxidation of ammonia. They observed that the mixed oxides had a higher activity than the single components and suggested that the redox properties of the mixed oxide composites are the main factor contributing to their activity. The Ce-Mn composite was later found to be active in the wet oxidation of polyethylene glycol and acetic acid, among other compounds [11] and, nowadays, this system is considered, by several authors [6, 8, 21], as a promising active catalyst for the wet air oxidation of organic pollutants. Despite the lack of information on the use of such material in the ozonation of organic compounds in the aqueous phase, it is possible that the activity of the Mn-Ce and Co-Ce composite oxides, in the mineralisation of aniline and sulfanilic acid, is related to their increased surface area and enhanced redox properties.

Despite the efficiency of manganese and cobalt oxides as ozonation catalysts, their major drawback is related to the metal leaching to solution. Even though manganese containing oxides present excellent results in the mineralisation of the studied compounds, measurable amounts of leached metal were observed during the experiments (see Appendix E). The catalysts containing cobalt are apparently more stable than those containing manganese, therefore being more promising as catalysts for the ozonation of organics in the aqueous phase. The following two chapters describe the main results obtained with cerium-based catalysts developed for the application in ozonation reactions.

7.3.3 Ozonation catalysed by metal oxides supported on activated carbon

In this part of the work, some metal oxides supported on activated carbon were tested in the ozonation of sulfanilic acid, aniline, and an azo dye (CI acid blue 113). The results obtained in terms of TOC removal are depicted in Figure 7.5.





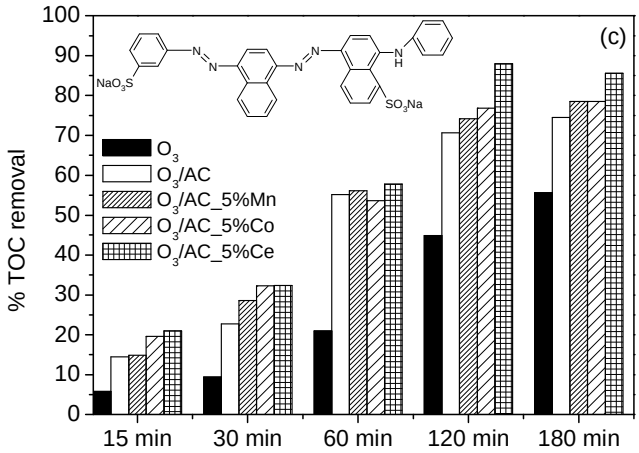


Figure 7.5 Evolution of TOC removal during single ozonation and ozonation catalysed by activated carbon or metal oxides supported on activated carbon (catalyst = 0.5 g/L) of: (a) sulfanilic acid (C_0 = 1 mM, pH_i = 3); (b) aniline (C_0 = 1 mM, pH_i = 6); (c) CI acid blue 113 (C_0 = 100 mg/L, pH_i = 5.5).

All the supported metal oxides evaluated showed a similar catalytic effect in the degradation of sulfanilic acid (Figure 7.5a) leading to mineralisation levels between 75 and 83% after 240 min of reaction, against 60% attained with the commercial activated carbon.

Aniline is easily oxidized by ozone leading to the formation of several oxidation by-products. The HPLC analysis showed a 96% conversion of aniline in approximately 15 min of single ozonation. However, in this short reaction period, only a small fraction of aniline, corresponding to 10% of TOC, was mineralised. Figure 7.5b shows a significant synergic effect between activated carbon and ozone in the mineralisation of the aniline solution [16]. Apparently, the introduction of metal oxides on the surface of activated carbon does not lead to a significant enhancement of the mineralisation of the aniline oxidation by-products. Nevertheless, for longer reaction periods (> 2 h), activated carbons impregnated with Mn or Ce seem to lead to higher TOC removals. Yet, the observed differences observed are quite small and can be within the experimental error.

The degradation of a solution of the acid dye CI 113 was also studied by ozonation catalysed by metal oxides supported on activated carbon. For comparative reasons the results obtained by single ozonation and ozonation in the presence of activated carbon are also presented (Figure 7.5c). Ozone is a strong oxidant which selectively attacks the chromophore groups of dye molecules. Therefore, colour removal is easily attained by single ozonation. However, the mineralisation rate of this type of compounds is generally low [22]. According to the experimental results, all the supported metal oxides enhanced the mineralisation of the acid dye, being the best results achieved with the catalyst containing cerium. Nevertheless, it must be stressed that activated carbon itself presents a significant catalytic effect, which seems to be slightly improved by the introduction of a metal oxide on its surface.

In general, supporting Mn, Co or Ce oxides onto activated carbon surface leads to an increment of the mineralisation of the studied compounds, particularly evident in the case of sulfanilic acid. According to the literature [23-26] and to previous work [12, 13, 16, 22] (see chapters 4, 5 and 6) on the ozonation of organic compounds in the presence of activated carbon, this material has been shown to act as ozonation catalyst. Even though reaction mechanisms are not fully clear, it is accepted that activated carbon promotes the mineralisation of organic compounds both through the decomposition of ozone into more reactive species such as $HO^{\cdot}$ that further react with organic species in the bulk, and through heterogeneous reactions occurring on the surface of the activated carbon. Considering the activity of activated carbon, it is clear that the major part of the catalytic effect observed with the supported metal oxides must be attributed to the support.

7.4 Conclusions

Single metal oxides, composite metal oxides and metal oxides supported on a commercial activated carbon were evaluated as ozonation catalysts for the mineralisation of selected organic compounds.

All the prepared metal oxides catalyse the ozonation of both sulfanilic acid and aniline, significantly increasing the mineralisation rate of the corresponding solutions, comparatively to single ozonation. The experimental results showed that intimate mixtures of metal oxides of Ce-Mn and Ce-Co, obtained by co-precipitation, are more efficient ozonation catalysts than the corresponding single

metal oxides, which might be related both to their higher surface areas and enhanced redox properties.

Metal oxides supported on activated carbon have been shown to be effective ozonation catalyst for the degradation of the mentioned aromatic compounds and an azo textile dye. Nevertheless, when comparing the respective results with those obtained with the commercial activated carbon, it should be notice that a significant part of the catalytic effect observed must be attributed to the support.

Both supported and massive cerium oxide showed interesting results in the catalytic ozonation of the selected organic compounds. Cerium oxide is insoluble in water and cerium catalysts seem to be more stable than those containing manganese or cobalt. The development of catalysts containing cerium oxide for the application in ozonation processes is the work described in the following chapters.

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8 A Novel Ceria-Activated Carbon Composite for the Catalytic Ozonation of Carboxylic Acids[1,2]

Ceria (Ce-O) and a novel ceria-activated carbon composite (AC_0-Ce-O) were prepared and tested as catalysts in the ozonation of two selected carboxylic acids, oxalic acid and oxamic acid, at acid pH. Ce-O showed an interesting catalytic effect, especially in the ozonation of oxalic acid. A strong synergic effect was observed for the AC_0-Ce-O composite in the case of oxalic acid, leading to the best results in the mineralisation of this compound. Both materials enhanced the removal of oxamic acid relatively to single ozonation. The Ce-O catalytic ozonation was shown to comprise bulk oxidation reactions occurring via $HO^{\cdot}$ radicals. In the case of the composite, both surface and bulk reactions are supposed to occur. Some considerations about the mechanisms are presented.

8.1 Introduction

Ozone is a powerful oxidant that selectively attacks molecules containing unsaturated bonds leading to the formation of saturated compounds such as aldehydes, ketones and carboxylic acids. Due to their low reactive nature towards ozone, these compounds tend to accumulate in water. Therefore, single ozonation is not sufficient to achieve a high mineralisation degree. To overcome this drawback, ozonation processes are being modified in order to increase their oxidising capability. Some studies show that several metals in solution or in the solid phase under various forms (salts of reduced metal, solid oxide, supported metal) may catalyse ozonation reactions, being able to destroy more recalcitrant pollutants [1]. Heterogeneous catalytic ozonation, which is one of the most attractive alternatives, aims to enhance the removal of more refractory compounds through the

[1] Based on PCC Faria, JJM Órfão, MFR Pereira, Cat Com 9 (2008) 2121-2126

[2] Additional data presented in Appendix F.

transformation of ozone into more reactive species and/or through adsorption and reaction of the pollutants on the surface of the catalyst [2]. The efficiency of the catalytic ozonation depends on the surface properties of the catalyst as well as on the solution pH and the chemical nature of the reactants. Results on the heterogeneous catalytic ozonation of particularly refractory substances have been previously reported. Oxides of transition metals, such as manganese [3], titanium [4] or cobalt [5], are amongst the most frequently studied ozonation catalysts.

The application of cerium-based catalysts in several processes, including wet air oxidation reactions [6-8], has been extensively studied. However, only a few studies have reported the use of cerium containing catalysts for the ozonation of organic compounds [9, 10]. Leitner et al. [9] have reported the use of CeO_2 as ruthenium support for the oxidation of succinic acid in aqueous solution and it was shown to have a slight catalytic activity in the removal of this carboxylic acid. Cerium (IV) possesses a high oxidizing ability and the cerium redox pair (Ce^{3+}/Ce^{4+}) catalysed ozonation was found to be effective for the mineralisation of phenol [10].

In the present work, we attempted the preparation of a cerium oxide/activated carbon composite for application in catalytic ozonation reactions. The goal is to test the catalytic activity of cerium oxide in ozonation reactions and to investigate a possible synergic effect between activated carbon and cerium oxide in the ozonation of organic compounds. Recently, the development of highly dispersed CeO_2 on activated carbon and the preparation of carbon nanotubes/cerium oxide composites have been reported in the literature [11, 12]. Activated carbon itself has been proved to be an efficient ozonation catalyst [13-16]. To the best of our knowledge, no results have been found in the literature reporting the use of activated carbon/cerium oxide composites in ozonation processes. In this study the catalytic activity of cerium oxide and cerium oxide/activated carbon composite was investigated in the ozonation of two selected carboxylic acids. Both oxalic and oxamic acids are common final oxidation products of several organic pollutants and are usually refractory to single ozonation. The results were compared with those obtained previously with the same activated carbon [15] used in the preparation of the composite. The catalysts were characterised by X-ray diffraction (XRD), scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) in order to correlate the catalysts activity with their chemical structure and surface properties.

8.2 Experimental

8.2.1 Materials

Oxalic acid (99%) and oxamic acid (96%) were obtained from Sigma-Aldrich. A commercial activated carbon, Norit GAC 1240 PLUS (sample AC_0), was used as received. Cerium oxide (sample Ce-O) was prepared by precipitation, according to the procedure described by Imamura et al. [7], using aqueous solutions of cerium (III) nitrate, Ce $(NO_3)_3.6H_2O$. In each batch, 200 mL of a sodium hydroxide 3 M solution was added drop wise to the metal salt solution (ca. 15 g/100 mL H_2O) under continuous stirring. The resultant precipitate was thoroughly washed with distilled water, dried at 100 ºC for 24 h and calcinated in air (50 cm^3 min^{-1}, measured at room T and P) at 450 ºC for 3 h. A composite of activated carbon and cerium oxide (sample AC_0-Ce-O) was prepared by a similar procedure as for sample Ce-O, where a given amount of activated carbon was dispersed in the nitrate solution before addition of NaOH. The nominal load of CeO_2 was expected to be ca. 50% wt. After precipitation, the suspension was shaked for 5 h at room temperature. Then, it was filtered and thoroughly washed and dried in an oven for 24 h at 100 ºC. This material was thermally treated at 450 ºC for 3 h under a flow of N_2 (50 cm^3 min^{-1}, measured at room T and P). The catalysts were sieved to a particle size of 100-300 μm prior to reaction studies.

The textural characterization of the materials was based on the corresponding N_2 equilibrium adsorption isotherms, determined at 77 K with a Coulter Omnisorp 100 CX apparatus. As reference, the BET surface areas (S_{BET}) of the samples were calculated. The relative amount of cerium oxide in the composite was determined by thermogravimetric analysis under air in a Mettler TA 4000 thermal analyser. The morphology and semi-quantitative elemental analysis of the catalysts were determined by SEM and energy dispersive X-ray spectroscopy (EDS) on a JEOL JSM 35C/Noran Voyager system. XRD spectra were recorded on a Philips X'Pert MPD diffractometer (Cu Kα = 0.15406 nm) and XPS was performed with a VG Scientific ESCALAB 200A spectrometer. XPS data corresponding to Ce 3d spectra was fitted using the software XPSpeak. To minimize the number of degrees of freedom of the curve fitting procedure, constraints on the binding energy (BE), full width at half maximum (FWHM) and peak areas were applied to each doublet pair.

8.2.2 Kinetic experiments

The removal of oxalic and oxamic acids from aqueous solutions was investigated in a slurry lab-scale reactor equipped with agitation and recirculation jacket (see Appendix A). For comparative purposes, both adsorption and ozonation experiments in the absence of catalyst were performed in the same system, under identical experimental conditions. The results were compared with those obtained with activated carbon. In each experiment the reactor was filled with 700 mL of each acid solution 1 mM at the natural pH, which was approximately 3. In the adsorption and catalytic ozonation experiments, 350 mg of catalyst (particle size = 100 - 300 μm) were introduced in the reactor. Ozone was produced from pure oxygen in a BMT 802X ozone generator. The experiments were performed at constant gas flow rate (150 cm^3 min^{-1}, measured at room T and P) and constant inlet ozone concentration (50 g Nm^{-3}). The concentration of ozone in the gaseous phase was monitored with a BMT 964 ozone analyzer. Ozone in the gas phase leaving the reactor was removed in a series of gas washing bottles filled with iodide potassium solution. The agitation was maintained constant at 300 rpm in order to keep the reactor content perfectly mixed and the temperature was set to 25 ºC.

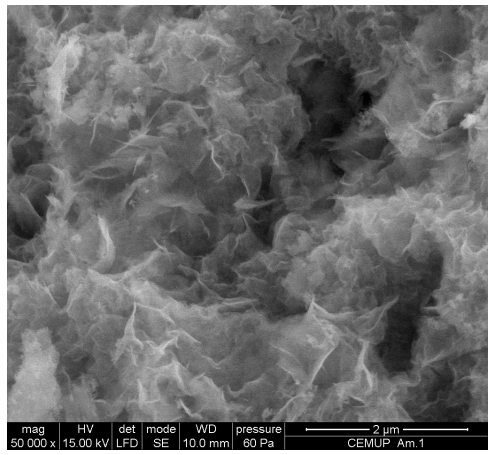
The concentration of both oxalic and oxamic acids was followed by HPLC using a Hitachi Elite Lachrom HPLC equipped with a diode array detector. The stationary phase was a YMC Hydrosphere C18 column (250 mm x 4.6 mm) working at room temperature, under isocratic elution with a mixture of water, acetonitrile and *o*-phosphoric acid at pH 2. Ammonium ion concentration was measured with a WTW NH500 ammonia-selective electrode.

8.3 Results and discussion

8.3.1 Catalysts characterization

Samples Ce-O and AC_0-Ce-O were analysed by SEM at different magnifications and the corresponding images are presented in Figure 8.1. EDS analysis of sample Ce-O confirmed the presence of cerium and oxygen.

(a)



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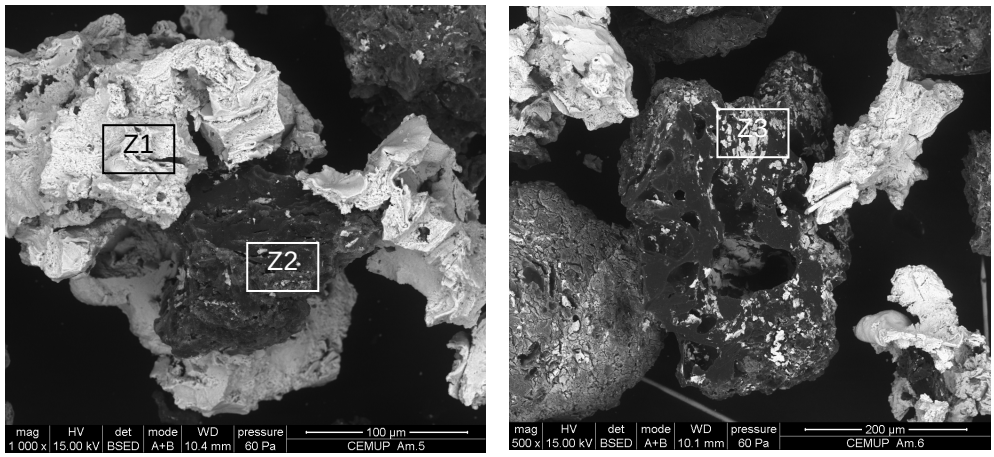

(b_1) (b_2) (b_3)

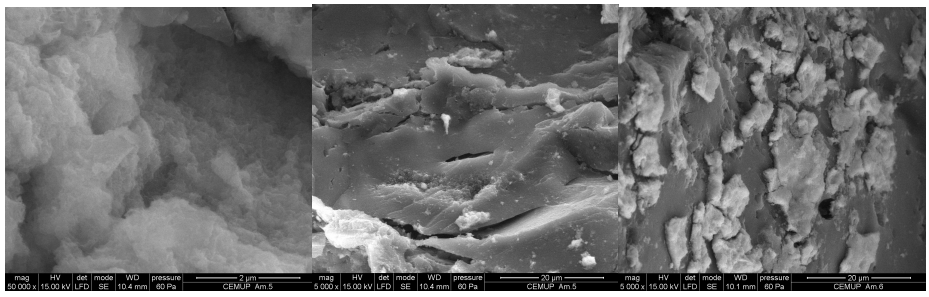

Figure 8.1. SEM images of samples Ce-O (a) and AC_0-Ce-O at different particles (b); Images (b_1), (b_2) and (b_3) correspond to magnifications of zones Z_1, Z_2 and Z_3, respectively.

SEM and EDS analyses of sample AC_0-Ce-O revealed the morphology and the semi-quantitative elemental composition of the particles of this composite material. In the same catalyst particle it is possible to identify Ce enriched zones (clear areas) (Z1) and activated carbon (dark areas) covered by cerium oxide in lesser or greater quantities (zones Z2 and Z3, respectively). Figure 8.1(b_1), Figure 8.1(b_2) and Figure 8.1(b_3) correspond, respectively, to higher magnification images of the mentioned zones. From the comparison between SEM images of fresh and spent catalyst, it was concluded that both have identical morphology. Even though activated carbon surface is partially oxidized by ozone [17], no major differences were observed in the morphology of Ce-O and AC_0-Ce-O after ozonation reaction.

Figure 8.2 shows the X-ray diffraction spectra of samples Ce-O and AC_0-Ce-O. In both samples, the dominant diffraction peaks are those characteristic of cerianite (CeO_2). Thermal analysis of sample AC_0-Ce-O revealed a cerium oxide average content of 45% wt.

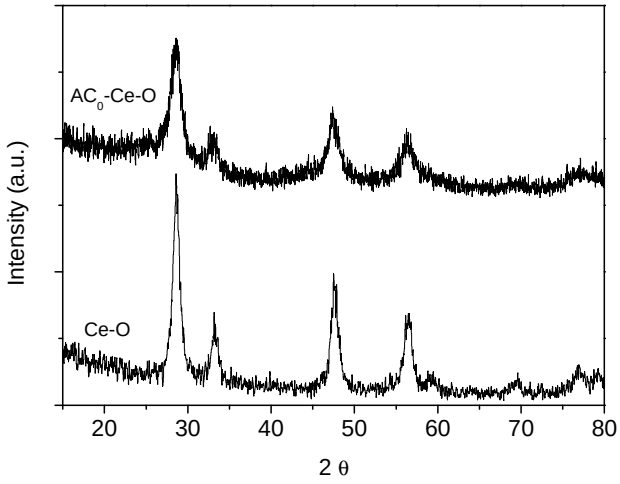

Figure 8.2. X-ray diffractograms of samples Ce-O and AC_0-Ce-O.

The oxidation states of surface cerium species on samples Ce-O and ACo-Ce-O were characterised by XPS analysis. According to the literature [18], the Ce 3d XPS spectra of Ce (IV) can be resolved into six features. If some Ce (III) species are present, then two more peaks and the corresponding satellites are added.

Furthermore, CeO_2 and Ce_2O_3 always show peaks at ~882.5 and ~916.5 eV as well as ~885.0 and ~903.7eV, which are considered fingerprints characterising Ce (IV) and Ce (III) oxides, respectively [19]. Although the Ce 3d spectra of both samples present the characteristic features of cerium (IV) oxide, the coexistence of both Ce (III) and Ce (IV) species must be considered in order to obtain a good fitting of the experimental data. Moreover, it has been shown by other authors [6, 19, 20] that cerium oxide prepared by precipitation from Ce (III) salt aqueous solutions can result in CeO_2 containing traces of Ce (III). The curves were fitted with eight peaks each, corresponding to four pairs of spin-orbit doublets, following the convention adopted by Burroughs et al.[21]. Three pairs of peaks (v, u; v'', u''; v''', u''') are characteristic of Ce (IV) and the pair (v', u') corresponds to one of the two pairs of spin-orbit doublets characteristic of the final state of the Ce(III) species [18, 22, 23]. The experimental and fitted Ce 3d spectra of samples Ce-O and AC_0-Ce-O are shown in Figure 8.3.

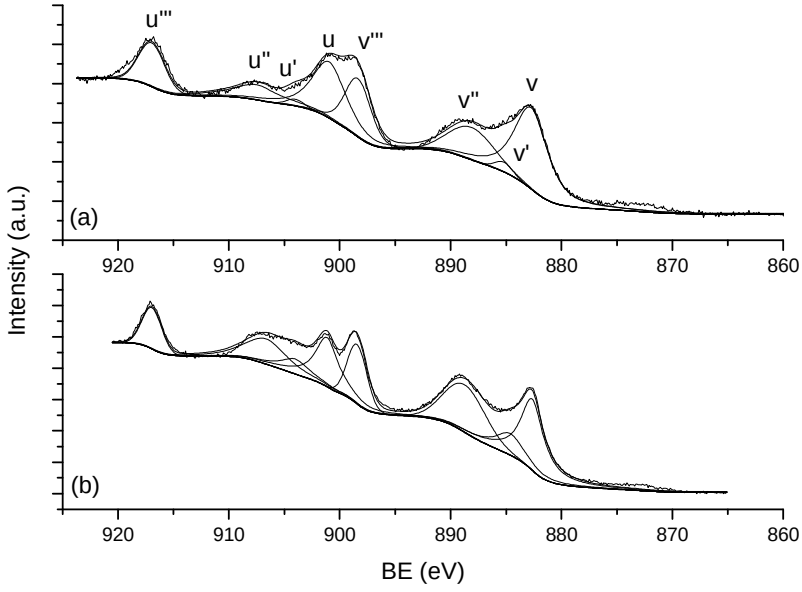

Figure 8.3. Experimental and fitted Ce 3d XPS spectra of samples (a) Ce-O and (b) AC_0-Ce-O.

The increase in the intensity of lines v' and u' in sample AC_0-Ce-O suggest the presence of a relatively higher amount of surface Ce (III) species comparatively to

sample Ce-O. The relative area of the Ce $3d_{3/2}$ peak at ca. 917 eV (u'''), characteristic of CeO_2 (it is absent in pure Ce_2O_3) has been used for semi-quantitative estimation of the relative amount of cerium present as Ce (IV). According to Shyu et al. [24], in pure CeO_2 this peak represents ca. 14% of the total area of Ce 3d spectrum. This ratio was calculated for both samples: for sample Ce-O the relative amount of Ce (IV) was 12.7%, while for sample ACo-Ce-O the calculated ratio was 9.0%, which is in agreement with the previous reasoning. In summary, according to the XPS results it is possible to conclude that the Ce (IV)/Ce (III) redox couple exists on the surface of the prepared ceria containing catalysts. The increased presence of Ce (III) in the ceria-activated carbon composite, relatively to sample Ce-O, may be explained by the transfer of electrons from the activated carbon basal planes to the metal oxide.

The textural characterization of the materials was based on the corresponding N_2 equilibrium adsorption isotherms determined at 77 K. The selected activated carbon has a BET surface area of 909 m^2/g. The complete characterization of this material is reported elsewhere [17] (see chapter 2). Samples Ce-O and AC_0-Ce-O have BET surface areas of 72 and 583 m^2/g, respectively.

8.3.2 Ozonation of oxalic and oxamic acid

Oxalic acid is known to be one of the most common final oxidation products of a large number of organic compounds. It is a small chain carboxylic acid highly refractory to ozonation. In a previous research, the ozonation of oxalic acid was shown to lead to complete mineralisation, i.e. no formation of organic intermediates were detected [15] (see chapter 5). A few catalysts have been reported to enhance the ozonation of oxalic acid in aqueous solution [3, 4, 25]. Among them, activated carbon was shown to be an effective catalyst to the mineralisation of this particular compound [15, 26]. Therefore, results obtained with activated carbon are presented here for comparative purposes.

The ozonation of oxalic acid was carried out at its natural solution pH, which was ca. 3. Both non-catalytic and catalytic ozonation in the presence of different catalysts are presented in Figure 8.4.

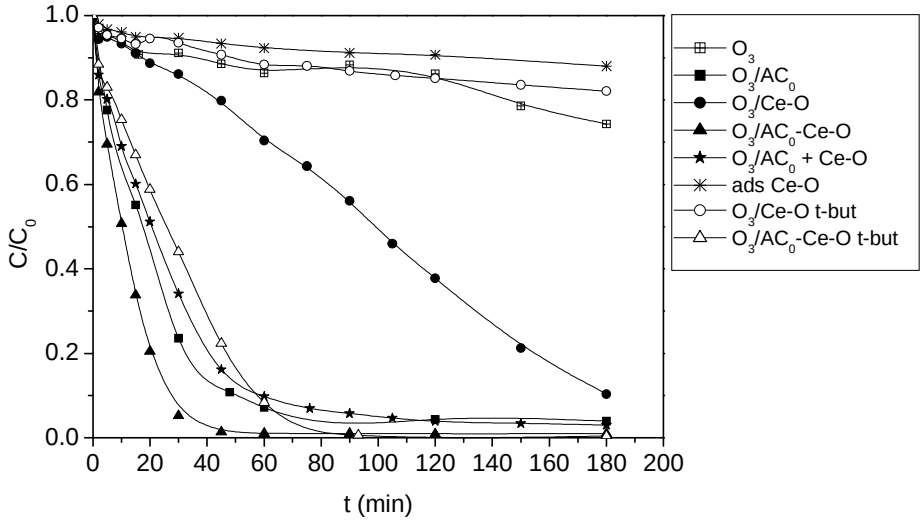

Figure 8.4. Evolution of the dimensionless concentration of oxalic acid at pH 3 during adsorption, catalytic and non-catalytic ozonation and effect of *tert*-butanol (C_0 = 1 mM, catalyst = 0.5 g/L, $C_{tert\text{-butanol}}$ = 10 mM).

The prepared cerium oxide has a significant catalytic effect leading to a 90% conversion of oxalic acid after 180 min of reaction, against approximately 25% removal obtained by single ozonation. Adsorption of oxalic acid in Ce-O has also been determined and accounts for 12% removal of this acid.

The ozonation of oxalic acid in the presence of sample AC_0-Ce-O showed excellent results, leading to nearly complete mineralisation of oxalic acid in approximately 45 min. In order to better understand this highly enhanced effect, an experiment using a physical mixture of activated carbon and cerium oxide (in the same proportion as in sample AC_0-Ce-O) was carried out. Considering that only approximately half of the mass of each component was used, a slight improved effect seems to be also obtained in this experiment. Nevertheless, this effect was clearly enhanced in the ceria-activated carbon composite, showing that an intimate mixture between cerium oxide and activated carbon results in a strong synergic effect for the ozonation reactions.

The low reaction rate constants reported in the literature for the ozonation of oxalic acid and their corresponding anions ($k < 0.04$ M^{-1} s^{-1} [27]) explain why such

compounds always accumulate as final products when organic aqueous solutes are ozonised in water. The compounds of low reactivity towards ozone may be oxidized by secondary oxidants such as hydroxyl radicals produced during the decomposition of ozone in aqueous solution. Actually, oxalic acid reacts with $HO^{\cdot}$ radicals at a much higher rate ($k \approx 10^6\ M^{-1}\ s^{-1}$ [28]). In order to verify whether the ozonation of oxalic acid in the presence of cerium oxide containing catalyst involves $HO^{\cdot}$ radicals, some experiments were carried out in the presence of *tert*-butanol, a well known $HO^{\cdot}$ radical scavenger. The results obtained for both Ce-O and AC_0-Ce-O catalyst are presented also in Figure 8.4.

The results show that the ozonation of oxalic acid catalysed by cerium oxide is strongly inhibited in the presence of *tert*-butanol. This experimental observation indicates that, in these conditions, the oxidation mechanism of oxalic acid occurs predominantly via $HO^{\cdot}$ radicals in the liquid bulk. It should be noted that these results are different from those obtained with activated carbon promoted ozonation in the same conditions [15] (see chapter 5), indicating different reaction mechanisms for the two catalysts. In the ozonation catalysed by AC_0-Ce-O, the presence of *tert*-butanol also inhibits the removal of oxalic acid. However, this effect was less pronounced than in the case of Ce-O, probably due to the contribution of activated carbon in the mineralisation of this carboxylic acid.

The oxidation of organic compounds containing nitrogen functional groups can also result in the formation of oxamic acid [29, 30], which is more refractory to oxidation than oxalic acid. In fact, oxamic acid was shown to be highly refractory towards ozonation at pH 3 [15] (see chapter 5). The results obtained for adsorption on Ce-O, single ozonation, and catalytic ozonation are depicted in Figure 8.5.

It has been previously found [15] (see chapter 5) that the simultaneous use of ozone and activated carbon resulted in a major increase in the removal of oxamic acid from solution. It was assumed that, at pH 3, the oxidation reaction occurred mainly on the surface of the activated carbon and no free $HO^{\cdot}$ radicals in the bulk solution were apparently involved in the conversion of oxamic acid.

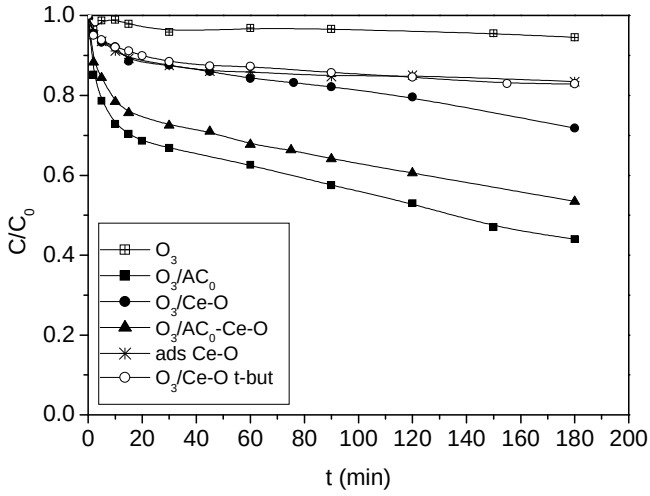

Figure 8.5. Evolution of the dimensionless concentration of oxamic acid at pH 3 (C_0 = 1 mM, catalyst = 0.5 g/L, $C_{tert\text{-butanol}}$ = 10 mM).

In the Ce-O catalysed ozonation, an enhanced removal rate of oxamic acid was observed from the first moments of reaction. However, after measuring the adsorption of oxamic acid on cerium oxide, an effective catalytic effect was only observed after 45 minutes of reaction. Up to this period, the decrease in oxamic acid concentration is coincident with that observed in single adsorption. As in the case of oxalic acid, the presence of a *tert*-butanol inhibited the ozonation of oxamic acid. Figure 8.5 shows that, in the presence of the radical scavenger, the amount of oxamic acid removed is similar to that obtained by adsorption. This evidences that the difference between the adsorption curve and the O_3/Ce-O curve is due to a contribution of oxidation via $HO^{\cdot}$.

Sample AC_0-Ce-O led to better results comparatively to sample Ce-O, which might be directly related to an increased surface area provided by the activated carbon contribution. Despite the mentioned effect, better results, in terms of oxamic acid removal, are attained with activated carbon. As previously reported [15] (see chapter 5), at pH 3, the ozonation of oxamic acid in the presence of activate carbon seems to occur via surface reactions. In this case a higher available surface appears to improve the removal of oxamic acid.

The mineralisation of oxamic acid catalysed by ceria and ceria-activated carbon composite results in the formation of NO_3^- and NH_4^+. Even though the conversion of oxamic acid is enhanced by sample AC_0-Ce-O relatively to Ce-O, much higher concentrations of NO_3^- and similar concentrations of NH_4^+ were detected during Ce-O catalysed ozonation. On the other hand, during the ozonation of oxamic acid in the presence of activated carbon no measurable amounts of NO_3^- and lower concentrations of NH_4^+ were detected (see Appendix F).

8.3.3 Considerations on the reaction mechanism

The ozonation of organic compounds involves a number of complex reactions and many mechanistic approaches have been presented in the literature. Generally it is assumed that in heterogeneous catalytic ozonation both surface and liquid bulk reactions can occur, involving molecular ozone, $HO^{\cdot}$ radicals and surface oxygenated radical species. It has been shown that the presence of a heterogeneous surface increases the dissolution of ozone [25] and acts as an initiator of the ozone decomposition reaction in aqueous phase. In general, the proposed mechanisms of ozonation catalysed by metal oxides assume that the adsorption of organic molecules and ozone takes place on the surface of the catalyst [31]. Ozone interaction with the metal oxide surface results in the formation of free radicals that can initiate a radical chain type reaction both on the surface of the catalyst and in the liquid phase, leading to the production of $HO^{\cdot}$ radicals [1, 25].

In the present work, the two ceria containing catalysts were shown to significantly enhance the ozonation of the selected compounds. It was experimentally demonstrated that the ozonation of both carboxylic acids catalysed by cerium oxide is almost completely inhibited when carried out in the presence of *tert*-butanol, which confirms that $HO^{\cdot}$ radicals play an important role in the reaction mechanism. On the other hand, adsorption of both carboxylic acids acid on Ce-O was clearly noted, thus it can be accepted as one of the reaction mechanism steps. According to the experimental data and based on the literature [1, 25], it can be assumed that the oxidation of the carboxylic acids occurs both on the surface of the cerium oxide between adsorbed species and in the liquid phase where the main oxidant species are predominantly $HO^{\cdot}$ radicals.

In the case of the prepared composite AC_0-Ce-O a strong synergic effect was observed between activated carbon and cerium oxide for the mineralisation of

oxalic acid. In a previous work it has been shown that activated carbon is an efficient ozonation catalyst for the removal of oxalic acid and, in less extent, of oxamic acid, at low pH [15] (see chapter 5). In that work, it was evidenced that both carboxylic acids were oxidized mainly on the surface of the activated carbon, since they are refractory to single ozonation and no significant effect was observed when adding *tert*-butanol to the system. In this ceria-activated carbon composite, activated carbon is supposed to play different roles. On one hand it provides a high specific surface area where both organic compounds and ozone can adsorb and react. On the other hand, the availability of free electrons on the surface of the activated carbon may contribute to formation of Ce (III) species (cf. XPS results), which are effective in the decomposition of ozone into $HO^{\cdot}$ radicals, in accordance with the reaction of ozone with Fe (II) as reported in the literature [1]. In fact, it was observed that the presence of *tert*-butanol partially inhibited the disappearance of oxalic acid during the ozonation catalysed by AC_0-Ce-O. Nevertheless, this effect was less pronounced than that observed with sample Ce-O, which is explained by the catalytic contribution of activated carbon.

8.4 Conclusions

The present work reports the preparation of cerium oxide based catalysts for the ozonation of organic compounds.

Ceria prepared by precipitation and a new ceria-activated carbon composite were tested in the ozonation of oxalic and oxamic acids. The presence of Ce (IV)/Ce (III) redox couple on the surface of the prepared ceria containing catalysts was evidenced by XPS analysis.

The results obtained in this study show that cerium oxide catalysts are effective ozonation catalysts for the removal of carboxylic acids. It is suggested that the oxide promotes the decomposition of ozone into $HO^{\cdot}$ radicals, which are the main oxidant species responsible for the oxidation of the compounds in the liquid phase.

In the case of oxalic acid, a strong synergic effect was observed between activated carbon and cerium oxide in the prepared composite. Accordingly, this sample showed excellent results in the mineralisation of that compound. The reaction mechanism is believed to comprise both surface reactions, similar to what occurs with activated carbon promoted ozonation and also liquid bulk reactions involving

$HO^{\cdot}$ radicals. It is assumed that the existence of delocalized electrons on the basal planes of the activated carbon contributes to the formation of Ce (III) species, which are active for the decomposition of O_3 into $HO^{\cdot}$ radicals.

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9 Mineralisation of Substituted Aromatic Compounds by Ozonation Catalysed by Ceria and a Ceria-Activated Carbon Composite[1]

Ceria (Ce-O) and a novel ceria-activated carbon composite (AC_0-Ce-O) were tested in the ozonation of three selected aromatic compounds: benzenesulfonic acid, sulfanilic acid and aniline. The catalysts performance was compared to that obtained with the commercial activated carbon. All the tested materials enhanced the mineralisation of the selected compounds. Generally, best results were achieved with the AC_0-Ce-O composite. A synergic effect between activated carbon and ceria in the prepared composite was confirmed in the mineralisation of a benzenesulfonic acid solution.

9.1 Introduction

Ozonation and several catalytic ozonation processes have been widely studied in the scope of wastewater treatment. Heterogeneous catalytic ozonation, which is one of the most attractive alternatives, aims to enhance the removal of recalcitrant compounds through the transformation of ozone into more reactive species and/or through adsorption and reaction of the pollutants on the surface of the catalyst [1].

Different supported and unsupported catalysts have been tested in the ozonation of several organic compounds [1]. Among the studied materials, activated carbon (AC) has been found to be a promising alternative to the treatment of wastewater containing dyes or other organic contaminants [2-8]. The application of cerium-based catalysts in several processes, including wet air oxidation reactions [9-11], has been extensively studied. However, only a few studies have reported the use of cerium containing catalysts for the ozonation of organic compounds [12-14].

[1] Based on PCC Faria, JJM Órfão, MFR Pereira, *submitted* (2008).

In a previous work [14] (see chapter 8), a ceria-activated carbon composite was prepared for the application in catalytic ozonation reactions. The results obtained showed that cerium oxide catalysts are effective ozonation catalysts for the removal of carboxylic acids (oxalic and oxamic acids). Experiments in the presence of the radical scavenger *tert*-butanol, supported the involvement of hydroxyl radicals ($HO^{\bullet}$) in the oxidation mechanism. It was suggested that cerium oxide promotes the decomposition of ozone into $HO^{\bullet}$ radicals, which are the main oxidant species responsible for the oxidation of the compounds in the liquid phase. A strong synergic effect was observed between activated carbon and cerium oxide in the prepared composite. In this case, the reaction mechanism is believed to comprise both surface reactions, similar to what occurs with activated carbon promoted ozonation [8] (see chapter 5) and also liquid bulk reactions involving $HO^{\bullet}$ radicals. It is assumed that the existence of delocalized π electrons on the basal planes of the activated carbon contributes to the formation of Ce (III) species, which are active for the decomposition of O_3 into $HO^{\bullet}$ radicals.

In this chapter, the study of the catalytic activity of cerium oxide and the ceria-activated carbon composite was extended to the ozonation of three selected aromatic compounds containing sulfonic and/or amine substituents. Sulfonated aromatic compounds as well as aromatic amines constitute a group of pollutants particularly difficult to eliminate from wastewater streams. Many of those, formed during the reduction of sulfonated azo dyes, are not susceptible to anaerobic or aerobic biodegradation and thus conventional biological treatments fail to mineralise these compounds [15, 16]. Some intermediates and final oxidation by-products of this class of pollutants are usually quite refractory to ozonation. Therefore, it is important to develop new catalysts capable of enhancing the mineralisation of such compounds.

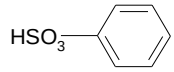
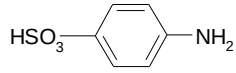
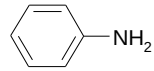
Benzenesulfonic acid, sulfanilic acid and aniline were used as model pollutants in the present study. The most refractory intermediates were followed along the experiments. In order to evaluate the performance of the composite, experimental results obtained with the activated carbon used in its preparation were included.

9.2 Experimental

9.2.1 Materials

Benzenesulfonic acid (BSA), sulfanilic acid (SA) and aniline were obtained from Sigma-Aldrich and used as received. Some properties of these compounds are presented in Table 9.1.

Table 9.1 Properties of the selected aromatic compounds.

		M (g/mol)	pKa
Benzenesulfonic Acid (BSA)		158.2	-2.36
Sulfanilic Acid (SA)		173.2	2.92*
Aniline		93.1	4.64*

* pKa corresponding to the group NH_3^+

Cerium oxide (sample Ce-O) was prepared by precipitation, according to the procedure described by Imamura et al. [10], using aqueous solutions of cerium (III) nitrate, $Ce(NO_3)_3.6H_2O$. In each batch, 200 mL of a sodium hydroxide 3 M solution was added drop wise to the metal salt solution (ca. 15 g/100 mL H_2O) under continuous stirring. The resultant precipitate was thoroughly washed with distilled water, dried at 100 ºC for 24 h and calcinated in air (50 cm^3 min^{-1}, measured at room T and P) at 450 ºC for 3 h. A composite of activated carbon and cerium oxide (sample AC_0-Ce-O) was prepared by a similar procedure as for sample Ce-O, where a given amount of activated carbon was dispersed in the nitrate solution before addition of NaOH. A commercial activated carbon, Norit GAC 1240 PLUS (sample AC_0), was used as received. After precipitation, the suspension was shaked for 5 h at room temperature. Then, it was filtered and thoroughly washed and dried in an oven for 24 h at 100 ºC. This material was calcinated at 450 ºC for 3 h under a flow of N_2 (50 cm^3 min^{-1}, measured at room T and P). The catalysts were sieved to a particle size of 100 - 300 μm prior to reaction studies.

The textural characterization of the materials was based on the corresponding N_2 equilibrium adsorption isotherms, determined at 77 K with a Coulter Omnisorp 100 CX apparatus. As reference, the BET surface areas (S_{BET}) of the samples were calculated. XRD spectra were recorded on a Philips X'Pert MPD diffractometer (Cu Kα = 0.15406 nm) and XPS was performed with a VG Scientific ESCALAB 200A spectrometer. XPS data corresponding to Ce 3d spectra was fitted using the software XPSpeak.

Thermal analysis of sample AC_0-Ce-O, carried on in a Mettler TA 4000 thermal analyser under a flow of air, revealed a cerium oxide average content of 45% wt. Samples Ce-O and AC_0-Ce-O have BET surface areas of 72 and 583 m^2/g, respectively. The selected activated carbon has a BET surface area of 909 m^2/g. The complete characterization of this material is reported elsewhere [17] (see chapter 2). According to the XRD results, the dominant diffraction peaks observed for both samples are those characteristic of cerianite (CeO_2). The presence of the Ce (IV)/Ce (III) redox couple on the surface of the prepared ceria containing catalysts was evidenced by XPS analysis. Additional detailed information on the characterization of the ceria based materials is reported elsewhere [14] (see chapter 8).

9.2.2 Kinetic experiments

The removal of BSA, SA and aniline from aqueous solutions was investigated in a slurry lab-scale reactor equipped with agitation and recirculation jacket (see Appendix A). For comparative purposes, ozonation experiments in the absence of catalyst were performed in the same system, under identical experimental conditions. In each experiment the reactor was filled with 700 mL of 1 mM solution at the natural pH of the compound. In the adsorption and catalytic ozonation experiments, 350 mg of catalyst (particle size: 100-300 μm) were introduced in the reactor. The temperature of the reactor was maintained at 25 ºC and the inlet concentration of ozone was 50 g/Nm^3. Additional experimental conditions and procedures are reported elsewhere [8] (see chapter 5).

The concentrations of the initial aromatic compounds and detected intermediates, including nitrates, were followed by HPLC using a Hitachi Elite Lachrom HPLC equipped with a diode array detector. The stationary phase was an YMC Hydrosphere C18 column (250 mm x 4.6 mm) working at room temperature. SA, aniline and the respective degradation compounds were analysed under isocratic

elution with a mixture of water, acetonitrile and *o*-phosphoric acid at pH 2.0. In the case of BSA, HPLC measurements were done under isocratic elution with a mixture of water, NaH_2PO_4 and *o*-phosphoric acid at pH 2.8. Ammonium ion concentration was measured with a WTW NH500 ammonia-selective electrode. The degree of mineralisation was followed by TOC analysis in a Shimadzu TOC-5000A Analyzer.

9.3 Results and discussion

The mineralisation of benzenesulfonic acid, sulfanilic acid and aniline was studied by ozonation catalysed by cerium oxide and activated carbon-cerium oxide composite materials, at the natural pH of each solution. For comparative purposes, the results obtained with the same activated carbon used in the preparation of the composite are also presented. The results obtained with each organic compound are presented separately in this section.

9.3.1 Benzenesulfonic acid

The ozonation of BSA catalysed by Ce-O and AC_0-Ce-O was carried out at pH 3.0, which is the natural pH of the solution. The experimental results obtained in terms of BSA and TOC concentrations are depicted in Figure 9.1. In order to facilitate the evaluation of the catalytic activities and the comparison between the different catalysts in the degradation of the reactant, the curves corresponding to BSA decay were fitted by a first order kinetic model. The respective apparent first order rate constants are presented in Table 9.2.

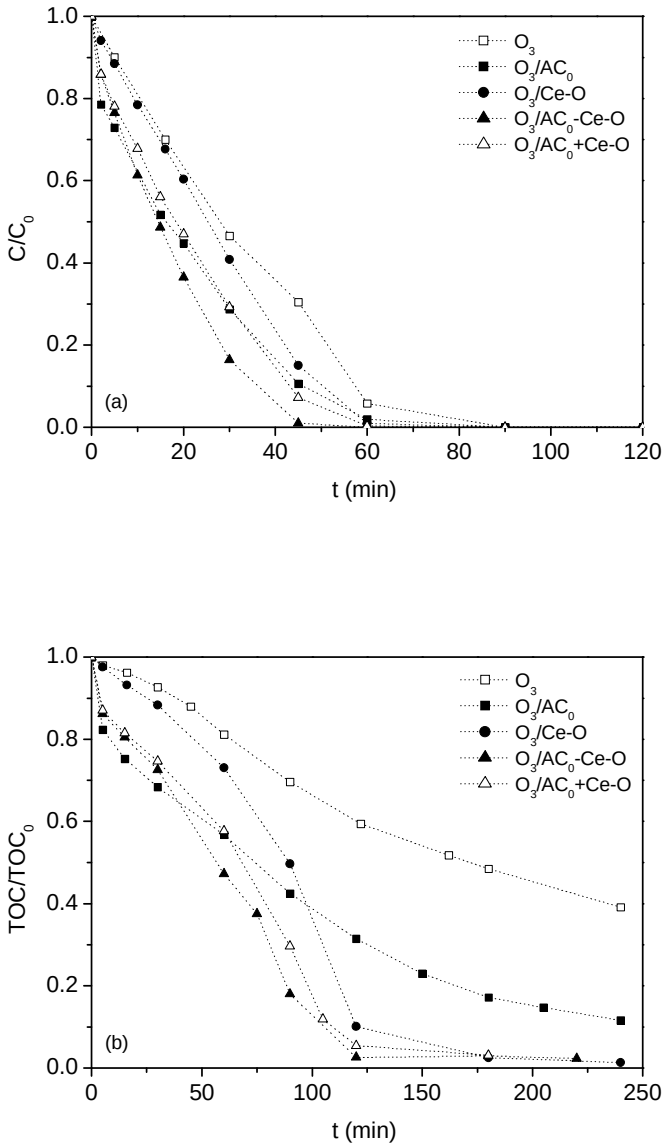


Figure 9.1 Evolution of the dimensionless BSA (a) and TOC (b) concentrations during non-catalytic and catalytic ozonation of BSA (C_0 = 1mM, pHi = 3.0, catalyst = 0.5 g/L).

Table 9.2 First order apparent rate constants of non-catalytic and catalytic ozonation of BSA, SA and aniline.

	BSA		SA		Aniline	
	k (min^{-1})	R^2	k (min^{-1})	R^2	k (min^{-1})	R^2
O_3	0.027	0.990	0.111	0.986	0.184	0.982
O_3/AC_0	0.046	0.983	0.145	0.990	0.268	0.990
O_3/Ce-O	0.029	0.984	0.128	0.991	0.204	0.982
O_3/AC_0-Ce-O	0.057	0.980	0.151	0.985	0.256	0.982

Under the experimental conditions used in this work, the conversion of BSA was enhanced by all the materials tested, which is confirmed by the calculated apparent first order rate constants. During the ozonation in the presence of activated carbon this enhanced effect is sometimes attributed to the adsorption capacity of this material. Nevertheless, the catalytic role played by activated carbon cannot be discarded [18]. In the case of the cerium oxide, the enhanced effect must be attributed mainly to a catalytic effect because BSA adsorption on this material is negligible (less than 8% of the initial concentration after 3 hours). Based on previous work [14] (see chapter 8), these results are due to the formation of $HO^{\bullet}$ radicals that are responsible for the enhanced oxidation of BSA. It has been found that the elimination of BSA is hardly accomplished only by molecular ozone attack [18] (see chapter 6). The substituent $-HSO_3$ is a strongly deactivating group since it decreases the electron density of the ring at the *ortho*- and *para*- positions through a resonance withdrawing effect. Hence these sites are less nucleophilic and, therefore, less prone to electrophilic attack by molecular ozone. According to Figure 9.1 and Table 9.2, there is a significant difference between the results obtained with samples AC_0 and AC_0-Ce-O. Even though the latter sample has a significantly lower surface area (583 m^2/g vs. 909 m^2/g), the catalytic effect in the elimination of BSA is more pronounced. This behaviour was attributed to the presence of cerium oxide. In order to understand the nature of the observed effect, another experiment using a physical mixture of activated carbon and cerium oxide (in the same proportion as in sample AC_0-Ce-O) was carried out. In fact, a slight synergic effect was also observed in this experiment. Nevertheless, this effect was enhanced in the ceria-activated carbon composite, showing that an intimate mixture between cerium

oxide and activated carbon is a benefit for the ozonation of BSA. Both Ce-O and AC_0-Ce-O have a remarkable effect in terms of TOC removal leading to nearly complete mineralisation of the compounds in solution after 2 hours. The combination of cerium oxide and activated carbon has an important synergic effect in the mineralisation of BSA.

According to the chromatograms obtained by HPLC, many intermediates arise from the ozonation of BSA but, under the experimental conditions used, their identification was not always possible to accomplish. In this work we were interested in identifying final oxidation products, which are usually saturated compounds quite refractory to oxidation. Oxalic acid was identified as one of the main reaction intermediates that persisted in solution throughout single ozonation, and was monitored during the reaction period. This particular carboxylic acid is known to be one of the most common final oxidation products of a large number of organic compounds in aqueous solutions. It is a small chain carboxylic acid, highly refractory to ozonation. The low reaction rate constants reported in the literature for the ozonation of oxalic acid and their corresponding anions ($k < 0.04\ M^{-1}\ s^{-1}$ [19]) explain why such compounds always accumulate as final products when organic aqueous solutes are ozonised in water. The compounds of low reactivity towards ozone may be oxidized by secondary oxidants such as hydroxyl radicals $HO^{\cdot}$, produced during the decomposition of ozone in aqueous solution. A few catalysts have been reported to enhance the ozonation of oxalic acid in aqueous solution. Among them, activated carbon was shown to be an effective catalyst to the mineralisation of this particular compound [8, 20]. In a previous work [14] (see chapter 8), cerium oxide containing catalysts were also found to be highly active for the mineralisation of oxalic acid.

As can be observed in Figure 9.2, the evolution of oxalic acid concentration in the presence of cerium oxide catalysts is quite different from that corresponding to single ozonation and activated carbon catalysed ozonation. In the former case the ozonation leads to faster and total disappearance of oxalic acid.

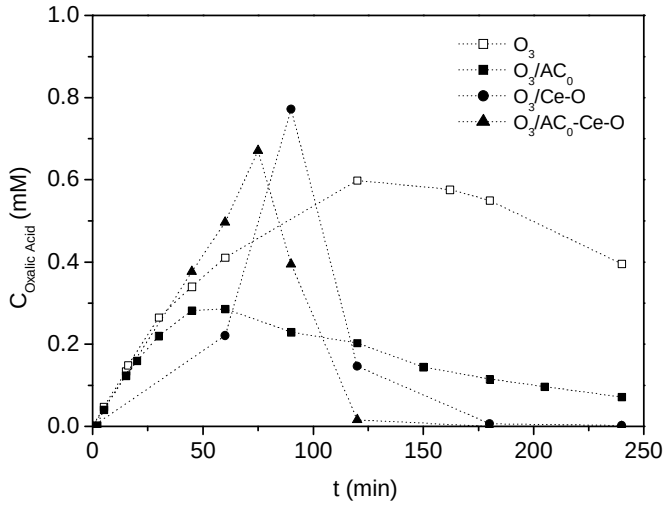


Figure 9.2 Evolution of oxalic acid concentrations during non-catalytic and catalytic ozonation of BSA (C_0 = 1mM, pHi = 3.0, catalyst = 0.5g/L).

After 180 min of single ozonation, oxalic acid concentration in solution represents ca. 36% of the measured TOC. In the presence of AC_0 the concentration of oxalic acid is lower and represents ca. 21% of the TOC in solution. In both cases there are other unidentified organic products responsible for the remaining TOC. On the other hand, the ozonation of BSA catalysed by Ce-O or AC_0-Ce-O results in the total elimination of oxalic acid formed and in the practically complete mineralisation of the organic compounds in solution (see Figure 9.1b). The mineralisation of BSA is accompanied by the release of the sulphur moiety which is, at least partially, converted into SO_4^{2-} [18].

9.3.2 Sulfanilic acid

The oxidation of SA was carried out at pH 3.3. The results obtained in non-catalytic and catalytic ozonation are depicted in Figure 9.3. In a previous work [18] (see chapter 6), SA was found to be easily oxidized by ozone. In fact, as it can be observed in Figure 9.3a, the complete removal of SA from solution occurs in approximately 20 minutes.

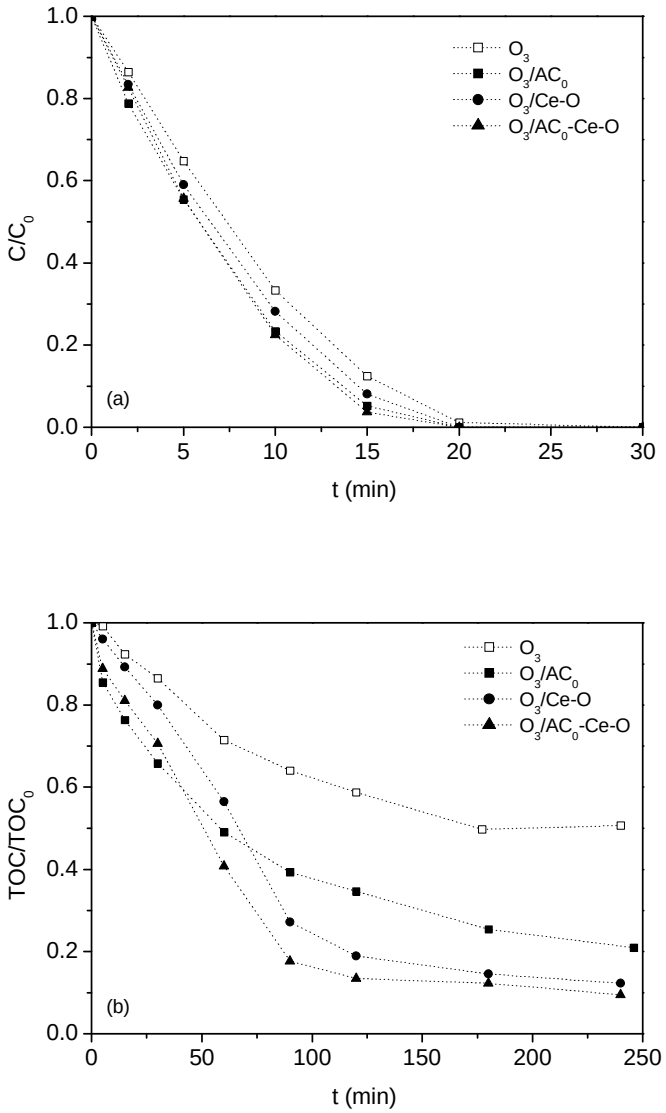


Figure 9.3 Evolution of the dimensionless SA (a) and TOC (b) concentrations during non-catalytic and catalytic ozonation of SA (C_0 = 1mM, pHi = 3.3, catalyst = 0.5g/L).

The addition of the Ce-O catalyst to the ozonation process slightly enhanced the elimination of SA, which can be confirmed by the apparent first order rate constants listed in Table 9.2. It should be pointed out that the amount of SA adsorbed on Ce-

O after 3 hours, represents less than 6% of the initial concentration. The catalytic activity of this material is evidenced especially when analyzing the TOC removal attained during the catalytic ozonation of SA. The composite material AC_0-Ce-O also presents an enhanced effect both in the elimination of SA and in the mineralisation of the dissolved organic compounds. In fact, the best results in TOC removal are obtained with this catalyst. After 120 minutes of reaction, the removal of TOC achieved with sample AC_0-Ce-O was 87% against 41% and 65% obtained with single ozonation and ozonation in the presence of activated carbon, respectively. Similarly to what was explained for BSA, the observed enhanced catalytic effect results from a cooperative action between activated carbon and cerium oxide. The former is thought to be able to promote the reduction of Ce (IV) to Ce (III), thus increasing the redox properties of the latter [14] (see chapter 8).

According to the apparent first order rate constants listed in Table 9.2, SA is less refractory to oxidation than BSA. The presence of the strong activating group -NH_2, increases the aromatic ring electron density through a resonance donating effect. The resonance allows electron density to be positioned at the *ortho*- and *para*-positions. Therefore, sulfanilic acid is susceptible of being attacked by molecular ozone preferentially at those sites. Nonetheless, higher TOC removals are attained for solutions of BSA (cf. Figure 9.1b and Figure 9.3b), since almost complete mineralisation of BSA is achieved in the presence of the cerium oxide catalysts. This must be related to the characteristics of the intermediates formed, which are expected to be more refractory in the case of SA. Actually, during the ozonation of sulfanilic acid, oxalic acid and oxamic acid are formed and the latter is an extremely recalcitrant carboxylic acid [8, 21]. These compounds are usually refractory to molecular ozone attack, but react more effectively with oxygenated radicals in the solution or on the catalysts surface [8] (see chapter 5).

The two mentioned carboxylic acids were found to be responsible for the greatest fraction of TOC in solution at longer reaction times. The concentrations of oxamic and oxalic acids were followed and the results obtained are depicted in Figure 9.4.

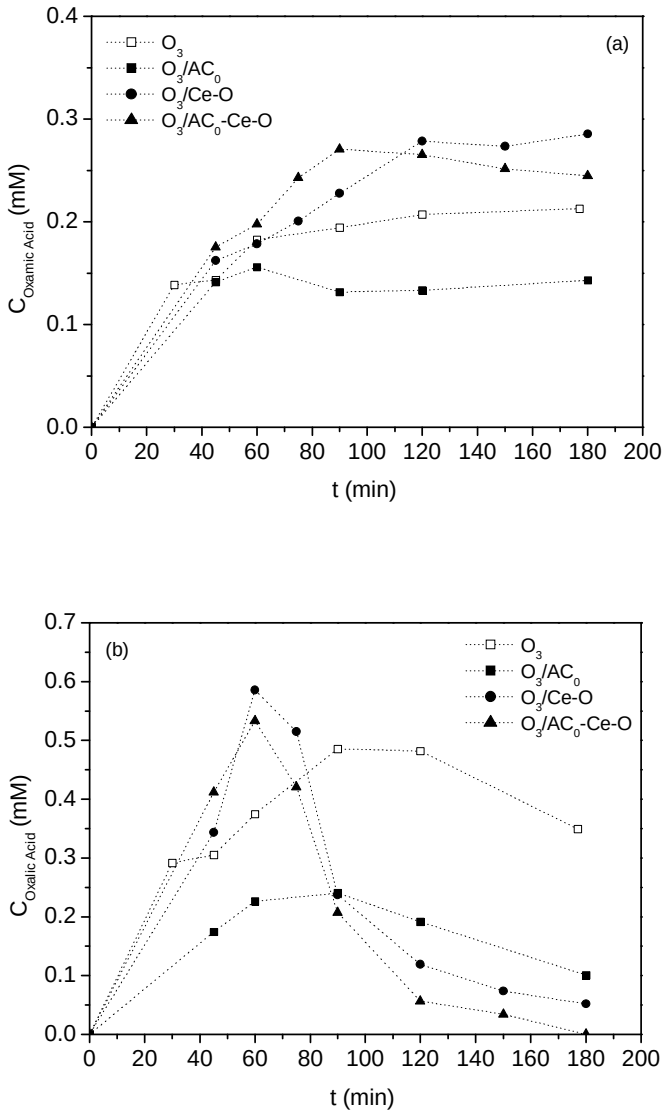


Figure 9.4 Evolution of oxamic (a) and oxalic (b) acids concentrations during non-catalytic and catalytic ozonation of SA (C_0 = 1mM, pHi = 3.3, catalyst = 0.5 g/L).

In a previous work [8] (see chapter 5), oxamic acid was found to be highly refractory to single ozonation. On the other hand, the ozonation catalysed by activated carbon enhanced the mineralisation of oxamic acid at low pH. As expected, during the oxidation of sulfanilic acid at pH 3.3, the presence of activated

carbon enabled the decrease of oxamic acid concentration in solution. Higher concentrations of oxamic acid were detected along time during the ozonation of SA catalysed by Ce-O or AC_0-Ce-O. Similarly to the observations during the ozonation of BSA, the curves of oxalic acid concentrations detected in the cerium oxide catalysed ozonation follow a different pattern from those of single ozonation and ozonation in the presence of activated carbon. Sample Ce-O leads to almost complete removal of oxalic acid after 3 hours, and in the case of sample AC_0-Ce-O, after the same reaction time, no oxalic acid was detected in solution. In this case, the amount of oxamic acid detected represents 66% of the TOC in solution, which means that only a relatively small fraction of TOC is due to unidentified products.

The mineralisation of SA is accompanied by the conversion of its initial nitrogen and sulphur moieties into inorganic ions. Both ammonium NH_4^+ and nitrate NO_3^- ions were detected and quantified during the ozonation of SA. Figure 9.5 depicts the evolution of the concentrations of NO_3^- during non-catalytic and catalytic ozonation. The concentrations of NH_4^+ found after 180 minutes of reaction are listed in Table 9.3, together with the nitrogen balance in solution at that time.

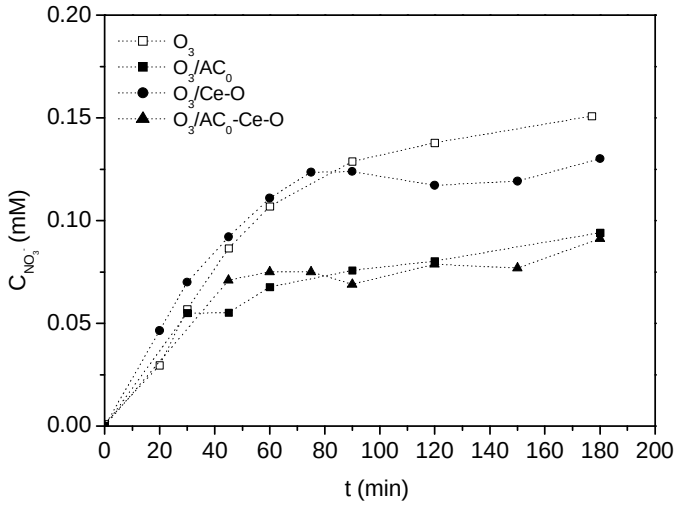


Figure 9.5 Evolution of NO_3^- concentration during non-catalytic and catalytic ozonation of SA (C_0 = 1mM, pHi = 3.3, catalyst = 0.5 g/L).

It was observed that the concentrations of NO_3^- were always lower whenever the ozonation of SA was carried out in the presence of activated carbon containing materials. This might be due to the formation of different N-containing intermediates and to the adsorption of some of those intermediates on the activated carbon. Moreover, the ozonation of such compounds in the presence of activated carbon may follow a route that does not lead to the potential formation of NO_3^-, as was reported for the catalytic ozonation of oxamic acid [8] (see chapter 5).

Table 9.3 Balance of nitrogen-containing species resultant from the oxidation of SA (Ci = 1mM, t =180 min).

System	NO_3^- (mM)	NH_4^+ (mM)	Oxamic Acid (mM)	N-Total (mM)
O_3	0.151	0.414	0.213	0.778
O_3/AC_0	0.094	0.416	0.143	0.653
O_3/Ce-O	0.130	0.455	0.286	0.871
O_3/AC_0-Ce-O	0.091	0.457	0.245	0.793

Regarding the formation of NH_4^+, no major differences were observed for the different catalytic systems studied. In a previous work [18] (see chapter 6), it was reported that there was a fast accumulation of NH_4^+, coincident with the disappearance of SA, probably due to the quick conversion of N-containing products in the early stage of the ozonation process. Several reasons can explain the fact that the nitrogen balance is not closed. The presence of unidentified nitrogen-containing species, especially in the cases of single ozonation and activated carbon catalytic ozonation must be taken into account. In the presence of activated carbon materials, the adsorption of the initial compound and the possible adsorption of nitrogenated oxidation by-products may also be considered. Additionally it is possible that the catalytic ozonation of SA may lead to the formation of gaseous nitrogen compounds, such as N_2 or nitrogen oxides.

9.3.3 Aniline

Ozonation is an efficient process for the degradation of compounds containing either an activated aromatic ring or double bonds, as ozone selectively attacks these chemical structures. The amino group ($-NH_2$) is electron donating and thus, it activates the aromatic ring by increasing its electronic density. Aromatic compounds, such as aniline, have a higher delocalisation of electrons and exhibit advanced reactivity towards ozone. In a previous work [22] (see chapter 4), aniline was found to be easily oxidized by single ozonation in a wide range of solution pH. In the present work, the ozonation of aniline was studied starting from a 1 mM aqueous solution at the natural pH, which is 6.4. Catalytic ozonation experiments were carried out using samples AC_0, Ce-O and AC_0-Ce-O. Both aniline and TOC decay were followed during 180 minutes and the obtained experimental data is depicted in Figure 9.6. The curves corresponding to aniline decay were fitted by a first order kinetic model. The respective apparent rate constants obtained are presented in Table 9.2.

Ozonation enables a fast decay of aniline concentration and, under the selected experimental conditions, the elimination of this compound from aqueous solution is achieved in less than 20 minutes. The simultaneous use of ozone and activated carbon improves the rate of aniline removal, which is explained by a sum of contributions of direct and indirect ozonation and adsorption on activated carbon. At pH 6.4, aniline is present in solution in its molecular form. It adsorbs on the AC through dispersive interactions between the free electrons of the AC surface and the electrons of the aromatic ring [23]. Thus, adsorption of aniline on activated carbon accounts for part of its removal from the solution. On the other hand, adsorption of aniline on Ce-O was found to be negligible and the elimination of aniline during Ce-O catalytic ozonation is not noticeably enhanced. However, when analyzing the TOC removal curves, the conclusions withdrawn are quite different. Sample Ce-O has a significant catalytic effect in the mineralisation of the solution. Best results are achieved with sample AC_0-Ce-O, which allows attaining an even higher mineralisation degree than activated carbon, after 90 minutes. Consequently, the role of these catalysts, as well as that of activated carbon, in the ozonation of organic compounds becomes crucial in the mineralisation of the oxidation by-products.

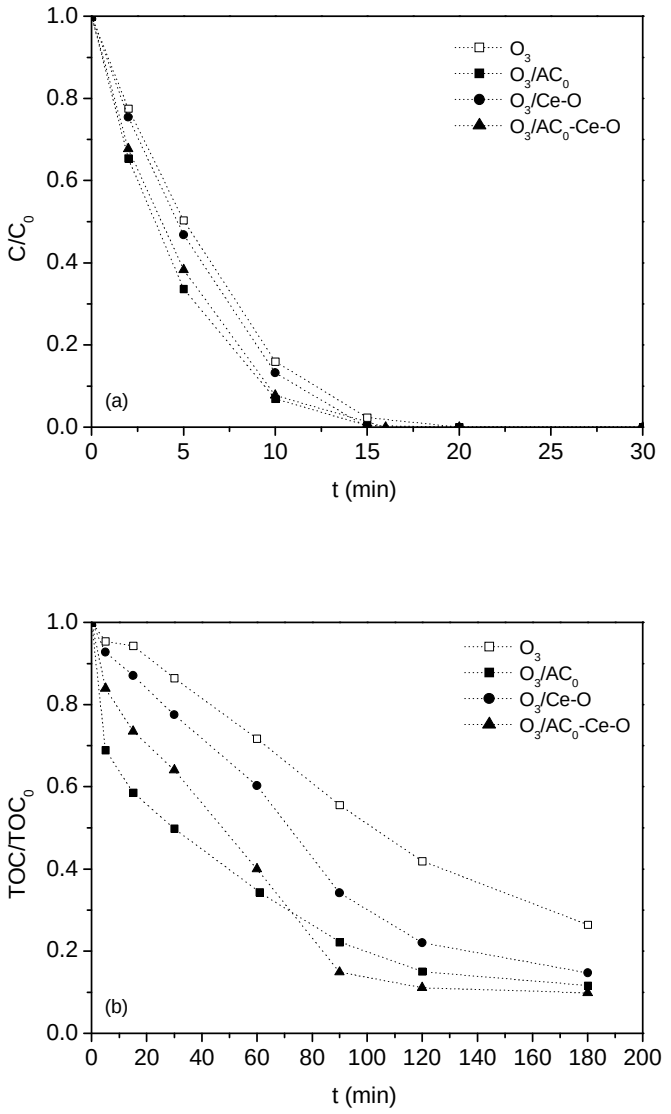


Figure 9.6 Evolution of the dimensionless aniline (a) and TOC (b) concentrations during non-catalytic and catalytic ozonation of aniline (C_0 = 1mM, pHi = 6.4, catalyst = 0.5 g/L).

The oxidation of aniline leads to the fast formation of intermediates that stay in solution for further mineralisation. In these work two classes of intermediates were identified: primary aromatic oxidation by-products, *ortho*- and *para*-aminophenol, and final oxidation products, oxalic and oxamic acids. Additionally inorganic ions, NO_3^- and NH_4^+, were also quantified. The formation of *ortho*- and *para*-aminophenol results from the hydroxylation of the aromatic ring in the *ortho* and *para* positions, respectively. After 15 to 20 minutes of reaction none of these products is present in solution. Though nitrobenzene was not followed in these reactions, it is known that this is also one of the primary intermediates of the oxidation of aniline [22]. Other aromatic compounds such as coloured condensation products are also formed in the early stages of aniline oxidation reactions but are further eliminated [24]. For longer reaction times, mainly saturated aliphatic compounds are expected to be found in solution. Under the experimental conditions used, oxamic and oxalic acids were identified as two of the carboxylic acids formed during the ozonation of aniline. The concentrations measured along time are depicted in Figure 9.7.

The evolutions of oxamic acid concentrations in the different processes are similar to those obtained in the ozonation of SA, i.e., lower concentrations of oxamic acid were found in the ozonation catalysed by activated carbon. On the contrary, the removal of oxalic acid is favoured by the presence of AC_0-Ce-O which, according to TOC data (Figure 9.6b), enhances the degree of mineralisation. After 180 minutes of reaction, the concentrations of these two carboxylic acids are responsible for a significant fraction of the TOC in solution. In non-catalytic ozonation and ozonation in the presence of activated carbon they represent, respectively, 42% and 45% of the measured TOC. In the case of the cerium containing catalysts, the residual concentrations of oxamic and oxalic acids account for 82% of the measured TOC for sample Ce-O while for sample AC_0-Ce-O they represent 97% of the measured TOC. In the latter case, oxalic and oxamic acids are, certainly the major final oxidation by-products of organic nature. This observation reinforces the high effectiveness of the ceria-activated carbon composite as ozonation catalyst.

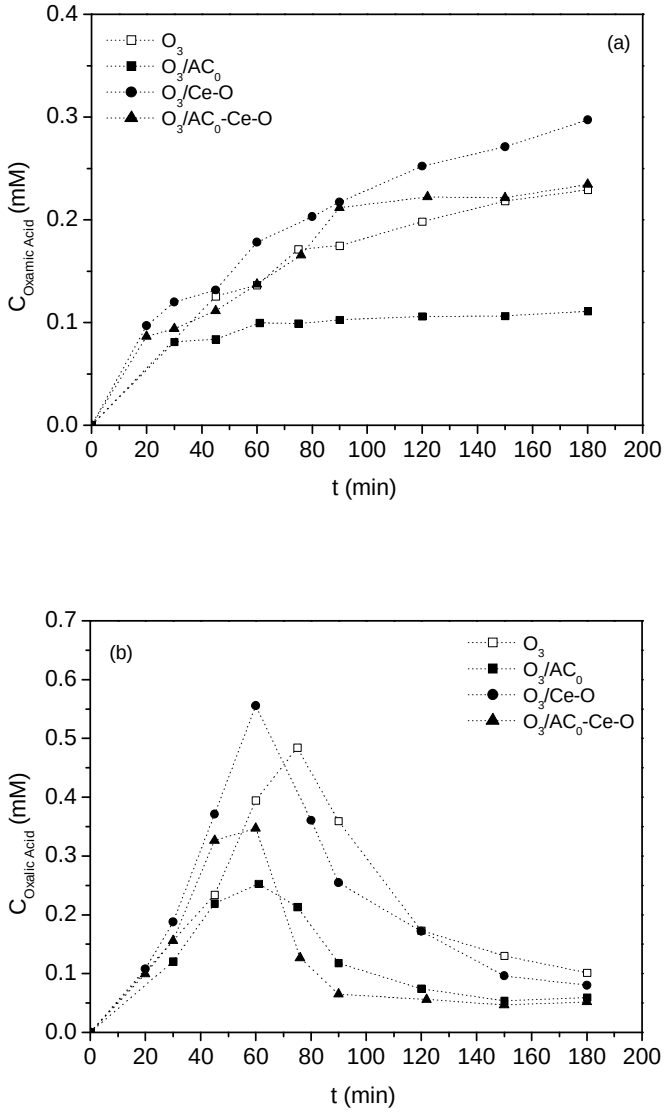


Figure 9.7 Evolution of oxamic (a) and oxalic (b) acids concentrations during non-catalytic and catalytic ozonation of aniline (C_0 = 1mM, pHi = 6.4, catalyst = 0.5 g/L).

During the ozonation, the nitrogen moiety of the aniline molecule is partially converted into inorganic nitrogen species, such as NH_4^+ and NO_3^-. The concentrations of NO_3^- detected in non-catalytic and catalytic ozonation of aniline

are shown in Figure 9.8. The concentrations of NH_4^+measured after 180 minutes of reaction are listed in Table 9.4, together with the nitrogen balance corresponding to the species present in solution.

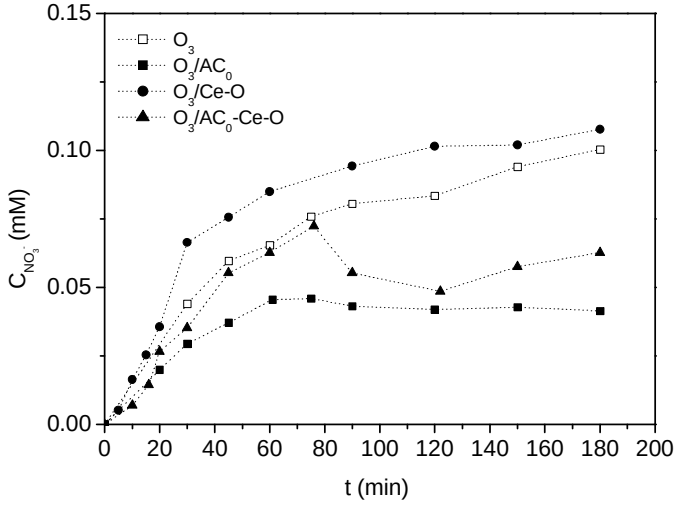


Figure 9.8 Evolution of NO_3^- concentrations during non-catalytic and catalytic ozonation of aniline (C_0 = 1mM, pHi = 6.4, catalyst = 0.5 g/L).

Table 9.4 Balance of nitrogen-containing species resultant from the oxidation of Aniline (Ci = 1mM, t = 180 min).

System	NO_3^- (mM)	NH_4^+ (mM)	Oxamic Acid (mM)	N-Total (mM)
O_3	0.100	0.492	0.229	0.821
O_3/AC_0	0.041	0.357	0.111	0.509
O_3/Ce-O	0.108	0.448	0.297	0.853
O_3/AC_0-Ce-O	0.063	0.370	0.234	0.667

The concentrations of NO_3^- follow a similar trend to that observed in the oxidation of SA. Apparently, in the presence of Ce-O, slightly higher concentrations of NO_3^- are formed, comparatively to single ozonation, which might be related to a higher

mineralisation of the compounds present in solution. Similar reasons presented for SA may account for the fact that the nitrogen balance is not closed.

9.3.4 Remarks on the individual catalysts roles and cooperative effect in the AC_0-Ce-O composite

In previous work, the simultaneous use of ozone and activated carbon was shown to enhance the mineralisation of several aromatic compounds [18, 22] (see chapter 4 and 6) as well as carboxylic acids [8] (see chapter 5), when compared to single ozonation and single adsorption, proving the existence of a catalytic reaction mechanism. It is generally accepted that the ozonation catalysed by activated carbon involves both surface and bulk reactions between the organic solute and oxygenated radical species.

More recently, both ceria and ceria-activated composite were found to be highly active catalysts for the ozonation of oxalic and oxamic acids [14] (see chapter 8). Particularly in the case of oxalic acid, a strong synergic effect was observed in the prepared composite. Both cerium oxide and activated carbon are active ozonation catalyst. The first was shown to enhance the decomposition of ozone into highly reactive species in solution, such as $HO^{\bullet}$, which participate in the oxidation reaction mechanism. Activated carbon has a more complex role. It catalyses the decomposition of ozone in the aqueous phase through the formation of surface oxygenated radical species as well as promoting the formation of $HO^{\bullet}$ in solution. The intimate mixture of cerium oxide and activated carbon is believed to promote the reduction of Ce (IV) to Ce (III) species, due to the existence of delocalized π electrons on the basal planes of the activated carbon. Therefore, the presence of the redox pair Ce (IV)/Ce (III) on the composite is believed to enhance its catalytic properties for the generation of $HO^{\bullet}$ radicals in the solution.

The synergic effect observed in the ceria-activated carbon composite for the mineralisation of the selected aromatic compounds is thus attributed to a combination of heterogeneous catalytic reactions, occurring preferentially on the surface of the activated carbon, and homogeneous reactions between the solutes and $HO^{\bullet}$ radicals resultant from the catalytic decomposition of ozone, mainly on cerium oxide.

9.4 Conclusions

The present work reports data on the ozonation of benzenesulfonic acid, sulfanilic acid and aniline catalysed by cerium oxide and a ceria-activated carbon composite material and compares the corresponding results with those obtained in the presence of activated carbon.

Both ceria containing catalysts were found to be highly effective ozonation catalysts. Comparatively to the performance of the commercial activated carbon, an enhanced mineralisation extent was achieved, particularly in the case of benzenesulfonic acid, where complete mineralisation was attained after 2 hours of reaction.

Catalytic and non-catalytic ozonation of sulfanilic acid and aniline results in the formation of extremely refractory final oxidation products, such as oxamic acid, which prevents attaining mineralisation degrees higher than 90%, within the total time defined for the kinetic experiments.

In the case of benzenesulfonic acid, the synergic effect was shown to be stronger for the composite material than for the physical mixture of cerium oxide and activated carbon, suggesting that an intimate mixture of those two materials is highly effective for the ozonation of organic compounds. The intimate mixture of activated carbon and cerium oxide is believed to promote the existence of the redox pair Ce (IV)/Ce (III), which seems to be active for the generation of $HO^{\bullet}$ radicals in the solution.

The mechanism of the ozonation catalysed by the ceria-activated carbon composite is believed to comprise both surface reactions, similar to what occurs with activated carbon promoted ozonation, and also liquid bulk reactions involving $HO^{\bullet}$ radicals, resultant from the catalytic decomposition of ozone on the surface of the activated carbon and mainly in the presence of cerium oxide.

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Part V

Catalytic Ozonation of Dyes and Textile Effluents

Catalytic ozonation is a promising technology for the treatment of industrial wastewater. Considering the liquid effluents originated in the textile industry, this process can be of particularly interest when used in the post-treatment of wastewater, envisaging its reuse.

The aim of this part of the thesis was to assess the suitability of selected catalytic ozonation systems for the treatment of textile effluents, in order to achieve extensive colour removal and high mineralisation rates. For that purpose, both simulated and real effluents were assessed. For the simulated effluents, a series of commercial textile dyes were selected. The influences of the concentration of dye, as well as the presence of carbonate species, were evaluated. In a final part of this work, two samples of real textile effluents, collected before and after biological treatment, were also tested. Ozonation experiments were performed with three catalytic systems: AC_0, Ce-O and AC_0-Ce-O. The experiments were conducted at laboratory scale in semi-batch mode and TOC measurement was the analytical method selected for the evaluation and comparison of the different systems.

10 Activated Carbon and Ceria Catalysts Applied to the Catalytic Ozonation of Dyes and Textile Effluents[1,2]

This study focuses on the application of catalytic ozonation processes for the decolourisation and mineralisation of coloured aqueous solutions. One acid azo dye, CI Acid Blue 113, and two reactive dyes, CI Reactive Yellow 3 and CI Reactive Blue 5, with azo and anthraquinone chromophores, respectively, were used as representative textile dyes. The catalytic activities of activated carbon, cerium oxide and a ceria-activated carbon composite were evaluated in the removal of the selected dyes. In all cases, complete decolourisation was achieved by single ozonation. The ceria-activated carbon composite allowed the highest removal of total organic carbon. For the lower dye concentrations, total mineralisation was achieved with the composite after 2 hours of reaction. The presence of sodium carbonate was found to partially inhibit the mineralisation of the solutions. The activity of the catalyst containing cerium was affected by the presence of carbonate and bicarbonate ions due to their scavenging effect towards hydroxyl radicals. All the catalytic systems were evaluated in the treatment of textile effluents, collected before or after conventional biological treatment. Catalytic ozonation was proven to be effective when used as tertiary treatment for bio-treated effluents.

10.1 Introduction

Intense colour is one of the main characteristics of textile wastewater originated from spent dye baths and dye rinsing operations. Besides the undesirable aesthetic impact caused by such effluents in receiving natural water courses, the persisting colour and the non-biodegradable nature of most of the textile dyes represent serious problems to the environment [1]. Conventional aerobic biological

[1] Based on PCC Faria, JJM Órfão, MFR Pereira, *to be submitted* (2008).

[2] Additional data presented in Appendix G.

treatments have proven insufficient to completely remove colour from textile plant effluents [2, 3]. Although there are several physical-chemical methods applied for colour removal, such as adsorption, membrane processes or physico-chemical treatments, chemical oxidation has become the method of choice due to its high efficiency and ease of operation. Ozonation of textile wastewater, spent and simulated dye baths has been focus of investigation [4-7]. Owing to its extremely high redox potential (E^0 = 2.07 V), ozone is one of the most effective oxidant agents used for this purpose. It reacts selectively with aromatic and unsaturated moieties [8], such as the chromophore structures of dye molecules, leading to fast decolourisation of the solutions. However, depending on the operational conditions and the nature of pollutants, the extent of mineralisation is usually insufficient. The oxidation of dyes and chemical auxiliaries present in textile effluents lead to the formation of intermediates that are frequently resistant to ozone attack. Such compounds of low reactivity towards ozone may be efficiently removed by oxidation via $HO^{\bullet}$ radicals [8]. Presently, advanced oxidation processes and catalytic oxidation are the main emerging routes for the removal of such compounds.

In order to enhance the efficiency of the ozonation processes, methods combining ozone with hydrogen peroxide, UV radiation, metallic ions or heterogeneous catalysts have been subject of intense research [9]. Heterogeneous catalytic ozonation aims to enhance the removal of more refractory compounds by the transformation of ozone into more reactive species and/or by adsorption and reaction of the pollutants on the surface of the catalyst [10]. Oxides of transition metals are trendy catalysts in ozonation processes [11-14], and activated carbon is also an attractive and promising alternative to the treatment of wastewater containing dyes or other organic contaminants [15-23]. In spite of the intense research, the development of highly effective catalysts for the application in ozonation processes, and the understanding of the inherent mechanisms are of great relevance.

In previous research [24, 25] (see chapters 8 and 9), the incorporation of cerium oxide and activated carbon was shown to be highly effective in the catalytic ozonation of a series of organic compounds. Experiments in the presence of the radical scavenger *tert*-butanol supported the involvement of hydroxyl radicals ($HO^{\bullet}$) in the oxidation mechanism.

The present work reports data on the catalytic ozonation of three commercial dyes from different chemical classes and distinct applications. One acid azo dye, CI Acid Blue 113 (AB113), and two reactive dyes, CI Reactive Yellow 3 (RY3) and CI Reactive Blue 5 (RB5), with azo and anthraquinone chromophores, respectively, were used as representative dyes. The effect of the dye concentration and the presence of bicarbonate (HCO_3^-) and/or carbonate (CO_3^{2-}) ions was assessed in non-catalytic and catalytic ozonation of RB5. With the main goal of validating the results obtained with the synthetic solutions, two textile effluents were used as case studies. The first one was collected after a conventional aerobic biological treatment. The second one is a global raw textile effluent collected in a vertical textile plant, at the homogenisation tank.

Three different materials, activated carbon (AC_0), cerium oxide (Ce-O), and a composite of activated carbon and cerium oxide (AC_0-Ce-O) were assessed. The performance of the catalytic systems was evaluated in terms of the decolourisation of the solutions and, mostly, in terms of the extent of mineralisation achieved, since this is an important parameter when evaluating the effectiveness of a given wastewater treatment .

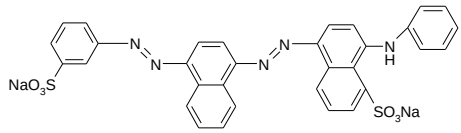
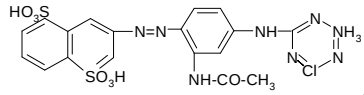
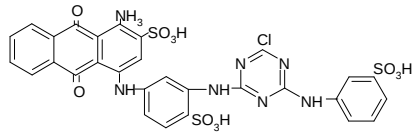
10.2 Experimental

10.2.1 Materials

In the present experimental study the synthetic coloured effluents were simulated considering three dyes belonging to different chemical classes: CI Acid Blue 113 (AB113), CI Reactive Yellow 3 (RY3) and CI Reactive Blue 5 (RB5). The molecules of the first two dyes have azo chromophores, while the latter possesses an anthraquinone chromophore group (Table 10.1). Regarding their application, the reactive dyes are used mostly in the dyeing of cellulosic fibres, and represent one of the most used classes of dyes. These dyes contain a reactive group, either a haloheterocycle, such as chlorotriazine, or an activated double bond, for instance of the vinylsulfone type, which forms chemical bonds with hydroxyl groups of the cellulosic fibres, when applied in alkaline medium. Reactive dyes have a low fixation degree compared to other types of dyestuff, since the functional group also bonds to water, becoming hydrolyzed, therefore inhibiting the reaction with the fibre [26, 27]. Acid dyes are normally used for dying wool, silk and some synthetic

fibres such as nylon. The corresponding molecules usually have a sulphonic or amino group that makes them soluble in water. These dyes are normally available as the corresponding sodium salts and, therefore, they are anionic in solution.

Table 10.1 Properties of the selected dyes.

Generic name (Commercial name)	Molecular Structure	Chemical class	λ_{max} (nm)
CI Acid Blue 113 (Erionyl Navy R)		Azo	566
CI Reactive Yellow 3 (Cibacron Yellow R)		Azo	411
CI Reactive Blue 5 (Cibacron Blue BR)		Anthraquinone	598

Two different textile effluents were assessed in this study. Textile effluent A (TEA) was collected in a collective wastewater plant, after conventional activated sludge treatment, but before the subsequent physical-chemical step. Therefore, it is representative of a global bio-treated textile wastewater. Textile effluent B (TEB) results from the mixture of all the liquid effluents produced in a textile dyeing mill. The main characteristics of each effluent will be presented in section 10.3.4. Before the ozonation experiments both samples were filtered under vacuum in order to remove suspended solids.

The preparation and characterization of the catalysts selected for this study (AC_0, Ce-O and AC_0-Ce-O) have already been presented and are described elsewhere [25, 28] (see chapters 2 and 8). Briefly, the cerium oxide catalyst (sample Ce-O) was prepared by precipitation, according to the procedure described by Imamura et al. [29], using aqueous solutions of cerium (III) nitrate, $Ce(NO_3)_3.6H_2O$. In each batch, 200 mL of a sodium hydroxide 3 M solution was added drop wise to the metal salt solution (ca. 15 g/100 mL H_2O) under continuous stirring. The resultant precipitate was thoroughly washed with distilled water, dried at 100 ºC for 24 h and calcinated in air (50 cm^3 min^{-1}, measured at room T and P) at 450 ºC for 3 h. A composite of

activated carbon and cerium oxide (sample AC_0-Ce-O) was prepared by a similar procedure as for sample Ce-O, where a given amount of activated carbon was dispersed in the nitrate solution before addition of NaOH. A commercial activated carbon, Norit GAC 1240 PLUS (sample AC_0), was used as received. After precipitation, the suspension was shaked for 5 h at room temperature. Then, it was filtered and thoroughly washed and dried in an oven for 24 h at 100 ºC. This material was calcinated at 450 ºC for 3 h under a flow of N_2 (50 cm^3 min^{-1}, measured at room T and P). The catalysts were sieved to a particle size of 100-300 μm prior to reaction studies.

Thermal analysis of sample AC_0-Ce-O, carried out in a Mettler TA 4000 thermal analyser under a flow of air, revealed a cerium oxide average content of 45% wt. Samples Ce-O and AC_0-Ce-O have BET surface areas of 72 and 583 m^2/g, respectively. The selected activated carbon has a BET surface area of 909 m^2/g, and its complete characterization is reported elsewhere [28] (see chapter 2). According to the XRD results, the dominant diffraction peaks observed for both samples are those characteristic of cerianite (CeO_2). The presence of the Ce (IV)/Ce (III) redox couple on the surface of the prepared ceria containing catalysts was evidenced by XPS analysis. Additional detailed information on the characterization of the ceria based materials is reported elsewhere [25] (see chapter 8).

10.2.2 Kinetic experiments and analytical methods

The removal of AB113, RY3 and RB5 from aqueous solutions was investigated in a slurry lab-scale reactor equipped with agitation and recirculation jacket (see Appendix A). Ozonation experiments in the absence of catalyst, and adsorption on activated carbon were performed in the same system, under identical experimental conditions. The synthetic coloured solutions were prepared by dissolving the desired amount of dye in distilled water. In every experiment the reactor was filled with 700 mL of each dye solution at a given concentration (50 mg/L or 300 mg/L), and at its natural pH (5 - 6). In the adsorption and catalytic ozonation experiments, 350 mg of catalyst (particle size = 100 - 300 μm) were used. The temperature of the reactor was maintained at 25 ºC and the inlet concentration of ozone was 50 g/Nm^3. Additional experimental conditions and procedures are reported elsewhere [23] (see chapter 5). The textile effluents were submitted to non-catalytic and catalytic ozonation under similar operational conditions.

The concentrations of each dye in the solutions were followed by UV-Vis spectrophotometry with a JASCO V-560 UV/Vis spectrophotometer. The UV-Vis spectra were measured at given time intervals. The degree of mineralisation was followed by TOC analysis in a Shimadzu TOC-5000A Analyzer. In selected experiments, HPLC analyses were performed using a Hitachi Elite Lachrom HPLC equipped with a diode array detector, in an attempt of identifying the final oxidation by-products. The stationary phase was an YMC Hydrosphere C18 column (250 mm x 4.6 mm) working at room temperature under isocratic elution with a mixture of water, acetonitrile and *o*-phosphoric acid at pH 2.0. Ammonium ion concentration was measured with a WTW NH500 ammonia-selective electrode.

10.3 Results and discussion

10.3.1 Mineralisation of synthetic coloured solutions

The mineralisation of the AB113, RY3, and RB5 solutions with an initial concentration of 50 mg/L was carried out by ozonation catalysed by AC_0, Ce-O and AC_0-Ce-O. Blank experiments of non-catalytic ozonation and adsorption on activated carbon were carried out for comparative purposes.

Non-catalytic ozonation is a powerful process for the degradation of dyes since ozone has the ability to selectively react with their chromophores, leading to high and fast colour removal. In the present work, all the dye solutions were effectively decolourised after very short reaction periods. In order to clarify the changes in the molecular and structural characteristics of the species resultant from the ozonation, the evolution of the UV-Vis spectra of each dye solution were recorded, as a function of time, and are depicted in Figure 10.1.

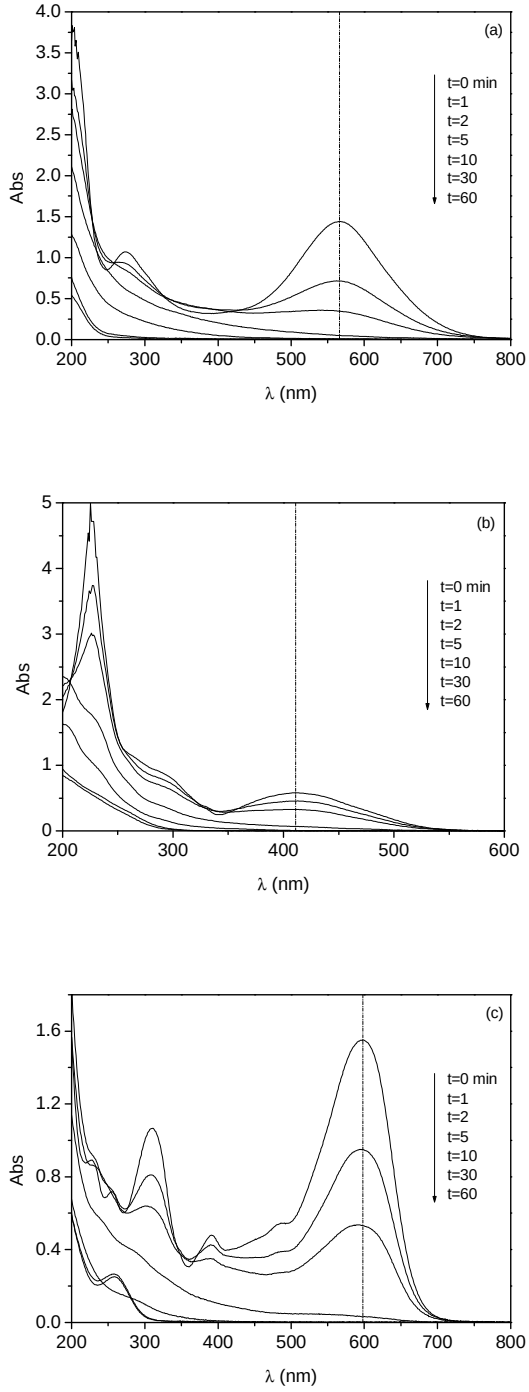


Figure 10.1 Evolution of UV-Vis spectra of (a) CI AB113, (b) CI RY3 and (c) CI RB5 during non-catalytic ozonation (C_0 = 50 mg/L).

The absorption spectra of AB113, RY3 and RB5 are characterised by one main band in the visible region, with the maximum absorption at 566, 411 and 598 nm, respectively, which is associated with the chromophores of the dye molecules. The evolution of the UV-Vis spectra during non-catalytic ozonation followed a similar trend for all dyes, i.e. the spectrum of each dye solution changes along time, with the disappearance of the band in the visible region, due to the ozone attack on the chromophore group, which determines the colour disappearance of the solution. In addition to the rapid bleaching effect, the decay of the absorbances in the UV region is considered an evidence of the degradation of the aromatic fragments of the dye molecules and their oxidation intermediates. Particularly, the absorbance at 254 nm is commonly associated with the presence of aromatic moieties.

The UV-Vis spectra recorded in the early stages of the catalytic ozonation of each dye are coincident, in all cases, with those obtained during non-catalytic ozonation. The decolourisation of the solutions during ozonation occurs mainly through the direct attack of ozone to the chromophore groups of the dye. This reaction is very fast and selective and, therefore, no major enhancements are achieved with the catalytic ozonation, concerning the decolourisation step (see Appendix G).

Experimental data corresponding to the decolourisation kinetics of AB113, RY3 and RB5 by non-catalytic ozonation and adsorption on AC_0 are depicted in Figure 10.2, in order to allow the comparison of the performance of the different dyes towards activated carbon adsorption and ozone attack. The colour of the solutions was assessed at the wavelength corresponding to the maximum absorption in the visible region of the UV-Vis spectrum of each dye (see Table 10.1).

Under the experimental conditions used in this work, the adsorption of the selected dyes is rather limited, as shown in Figure 10.2. In fact, the RY3 dye has a very low affinity towards activated carbon. After 120 min, the removal of AB113 and RB5 by adsorption on AC_0 was ca. 18% and 11%, respectively. These values are in agreement, within the experimental error, with those obtained in the TOC measurements.

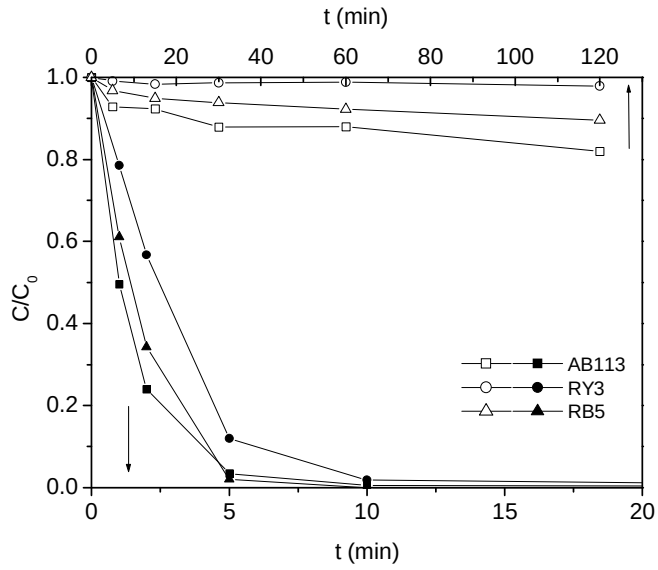


Figure 10.2 Kinetics of the non-catalytic ozonation (filled symbols) and adsorption on AC_0 (open symbols) of AB113, RY3 and RB5 at the natural pH of the solutions (C_0 = 50mg/L, AC_0 = 0.5 g/L).

The presented data show that adsorption is not effective for the decolourisation of these solutions. On the other hand, single ozonation allows a fast colour removal in short reaction times (less than 10 minutes). Comparing the experimental data corresponding to the colour removal kinetics of the three dyes, it was observed that the decolourisation rate of RY3 was inferior to that of AB113 or RB5. After 5 min of single ozonation the colour removal obtained for the solutions of AB113, RY 3 and RB5 was ca. 97, 88 and 98%, respectively. During this period, the colour removal achieved by adsorption on AC_0 varied between less than 1% for RY3 and 7% for AB113. Consequently, the contribution of the adsorption on activated carbon to the decolourisation step during the ozonation catalysed by AC_0 may be considered negligible.

Nevertheless, activated carbon is expected to play an important role in the adsorption of some reaction intermediates as well as in catalysing their oxidation, as it will be discussed later. The ozonation of the coloured solutions leads to the fragmentation of the dye molecules into smaller organic compounds that remain in the solution for further oxidation. When comparing the results obtained for the

mineralisation of the solutions, it was found that the intermediates obtained from the oxidation of the selected reactive dyes were more refractory to single ozonation than those corresponding to the acid dye, as shown in Figure 10.3. The most refractory to mineralisation is the RB5 dye, which belongs to the anthraquinone class.

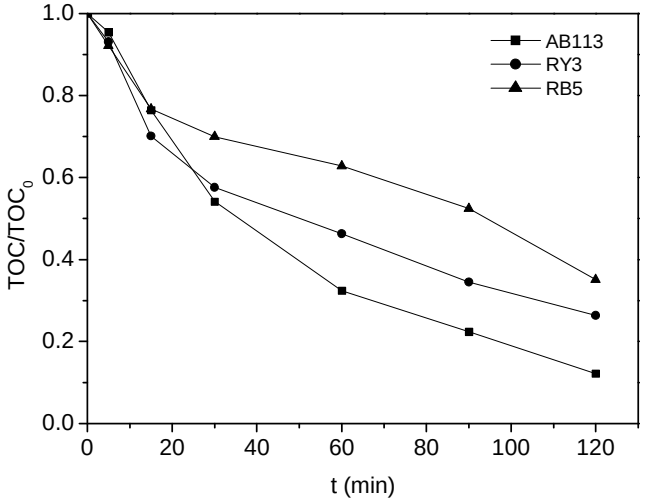


Figure 10.3 Evolution of dimensionless TOC during non-catalytic ozonation of AB113, RY3 and RB5 at the natural pH of the solutions (C_0 = 50 mg/L).

The ozonation of aromatic compounds usually leads to the formation of numerous intermediate such as aldehydes, ketones and carboxylic acids that tend to accumulate in solution due to their low reactivity towards ozone [30]. Such compounds may be oxidized by secondary oxidants, such as hydroxyl radicals, produced during the decomposition of ozone in aqueous solution [8]. In the scope of heterogeneous catalytic ozonation, refractory compounds are mineralised by the transformation of ozone into more reactive species and/or by adsorption and reaction of the pollutants on the surface of the catalyst [9].

Even though the decolourisation of the synthetic coloured solutions was not visibly enhanced by the studied catalytic systems, entirely different results were observed when analyzing the extent of the mineralisation achieved during catalytic ozonation. The kinetic data corresponding to the evolution of TOC during the catalytic

ozonation of AB113, RY3 and RB5 are presented in Figure 10.4, Figure 10.5 and Figure 10.6, respectively.

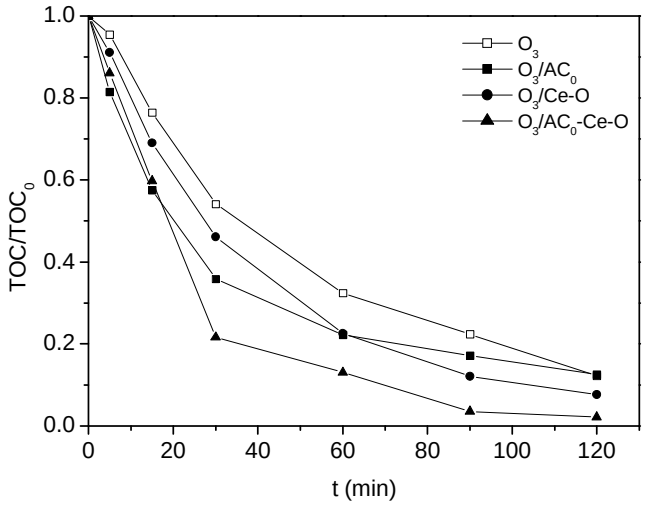


Figure 10.4 Evolution of dimensionless TOC during non-catalytic and catalytic ozonation of AB113 (C_0 = 50 mg/L, pHi = 5.8).

The acid dye AB113 was found to be the less refractory compound among the studied dyes. Non-catalytic ozonation allowed the removal of 88% of TOC within 120 min of reaction. Nonetheless, the mineralisation of the solution was visibly enhanced by all the catalytic systems, as shown in Figure 10.4. Activated carbon accelerated the mineralisation of the solution, yet the TOC removal rate seems to decrease after 60 minutes of reaction. Cerium oxide was shown to be active and the best results were achieved with the AC_0-Ce-O composite. Up to the first 15 minutes of reaction, the results obtained with AC_0 and AC_0-Ce-O were very similar. After that period there was a significant improvement in the removal of TOC obtained with the composite, leading to a higher mineralisation degree.

A very similar trend was observed for all the studied dyes. In the case of RY3 the simultaneous use of ozone and activated carbon led to an enhanced TOC removal when compared to single ozonation (Figure 10.5). As previously shown, RY3 has very little affinity towards activated carbon; therefore, the enhanced results may be

attributed to the catalytic effect of activated carbon mainly in the oxidation of intermediate products.

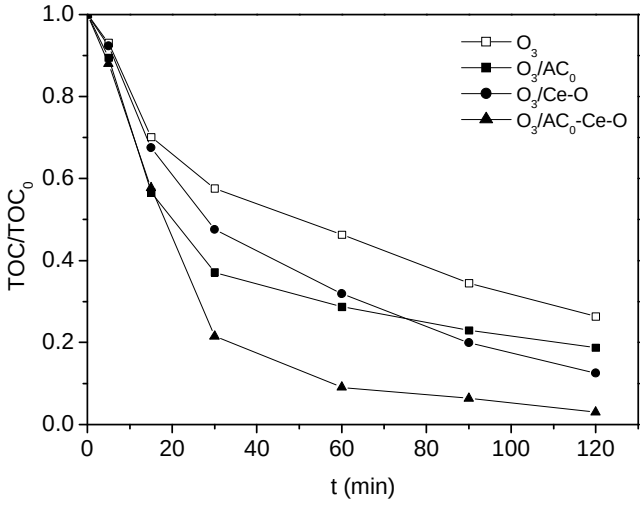


Figure 10.5 Evolution of dimensionless TOC during non-catalytic and catalytic ozonation of RY3 (C_0 = 50 mg/L, pHi = 5.8).

Comparatively to non-catalytic ozonation, the simultaneous use of ozone and activated carbon promoted an increase of 20% in the TOC removal of the solution, after 30 minutes. Also in this case, the highest mineralisation extent was obtained with the activated carbon-ceria composite. After 30 minutes of reaction, the TOC removal achieved was 78% against 42% obtained by single ozonation. Sample AC_0-Ce-O allowed nearly total mineralisation of the solution after a longer reaction period.

The reactive blue dye RB5 was shown to be the most refractory towards single ozonation and the biggest differences between non-catalytic and catalytic ozonation was observed in this case (Figure 10.6). After 30 minutes of reaction, the mineralisation extent obtained in non-catalytic ozonation was only about 30%. The addition of the activated carbon to the process approximately doubled the percentage of TOC removed. A remarkable enhancement in the mineralisation degree is obtained during the ozonation catalysed by the composite AC_0-Ce-O.

After 30 minutes, less than 14% of the initial TOC is present in solution and total mineralisation is achieved in less than 2 h of reaction.

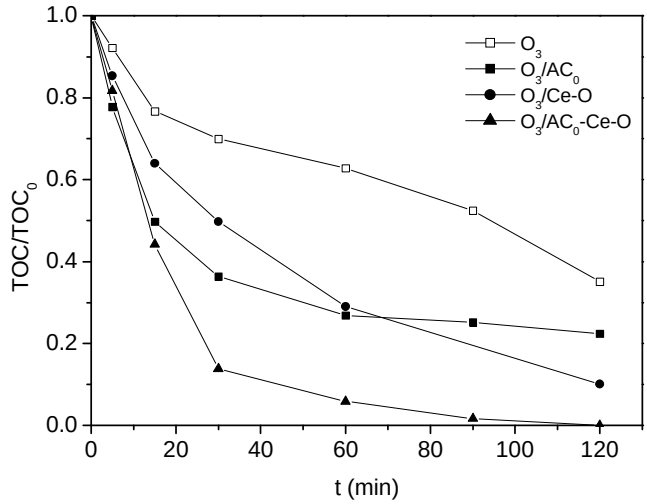


Figure 10.6 Evolution of dimensionless TOC during non-catalytic and catalytic ozonation of RB5 (C_0 = 50 mg/L, pHi = 5.6).

In all cases, cerium oxide was found to be an efficient ozonation catalyst and higher mineralisation degrees were achieved comparatively to the performance of activated carbon, but only for longer reaction periods (higher than ca. 60 min). Superior initial reaction rates are observed for the TOC removal during ozonation catalysed by both AC_0 and AC_0-Ce-O. This observation suggests a reaction mechanism distinct from that of cerium oxide catalytic ozonation. The latter is dependent of the formation of $HO^{\bullet}$ radicals [25] (see chapter 8), while the former namely comprises surface reactions on the activated carbon, as reported in a previous work [23] (see chapter 5). It was suggested that cerium oxide promotes the decomposition of ozone into $HO^{\bullet}$ radicals, which are the main oxidant species responsible for the oxidation of the compounds in the liquid phase. A strong synergic effect was observed between activated carbon and cerium oxide in the AC_0-Ce-O composite. The reaction mechanism is believed to comprise both surface reactions, similar to what occurs with activated carbon promoted ozonation and also liquid bulk reactions involving $HO^{\bullet}$ radicals. It was assumed that the existence of delocalized electrons

on the basal planes of the activated carbon contributes to the formation of Ce (III) species, which are thought to be necessary for promoting the decomposition of O_3 into $HO^{\cdot}$ radicals by redox reactions on the catalyst surface involving the pair Ce(III)/Ce(IV).

During single ozonation, the pH of the solutions drops to a value between 3.5 and 4, which is explained by the formation of by-products of acidic nature, such as small chain carboxylic acids. In the presence of the composite AC_0-Ce-O, the final pH of the solutions is usually higher, especially in the cases of AB113 (pH = 5.8) and RB5 (pH = 5.1), approximating the pH values of the initial solutions. These observations together with the TOC measurement confirm a highly efficient elimination of most of the oxidation by-products.

Previously, it was observed that the three dyes behaved in a different way towards non-catalytic ozonation, being RB5 the most refractory compound. When comparing the results obtained during catalytic ozonation, different conclusions were withdrawn. No major differences were observed in terms of TOC removal among the three catalysts used (see Appendix G). In fact, for the most promising catalytic system O_3/AC_0-Ce-O, a slightly faster mineralisation was observed for the anthraquinone dye, which is probably related to the nature of the intermediates formed. Even though those are resistant to ozone attack, they are mineralised during catalytic ozonation, due to the existence of less selective and highly oxidant species, as is the case of $HO^{\cdot}$ radicals, and to the catalytic oxidation occurring on the surface of the composite. These observations suggest that the results obtained with the catalytic ozonation systems are less influenced by the type of the coloured solutions than non-catalytic ozonation.

10.3.2 Effect of dye concentration in the catalytic ozonation of RB5

Depending on the type of dyes and dyeing processes used, dye concentrations of 0.01 g/L up to 0.25 g/L have been cited as being present in dyehouse effluents [26]. Reactive dyes have fairly low fixation levels, which may vary in the range of 50-90%, resulting in strongly coloured spent dyebaths. In spite of the deep colouration caused by very small concentrations of dyes, their contribution to the organic content of the solution is relatively low. In this work, the initial TOC content of the 50 mg/L solutions of the selected dyes was within 11-17 mgC/L. In order to study the influence of the concentration of dye in the ozonation process, a solution of 300

mg/L of RB5, with a corresponding TOC of 66 mgC/L, was prepared. A higher initial concentration of TOC was expected to allow a more accurate assessment of the performance of the different catalytic systems.

Both single ozonation and ozonation catalysed by AC_0, Ce-O and AC_0-Ce-O were carried out. The evolution of the UV-Vis spectra was recorded along time, and the colour of the solution was assessed at 598 nm. The kinetic data corresponding to decolourisation by ozonation is depicted in Figure 10.7.

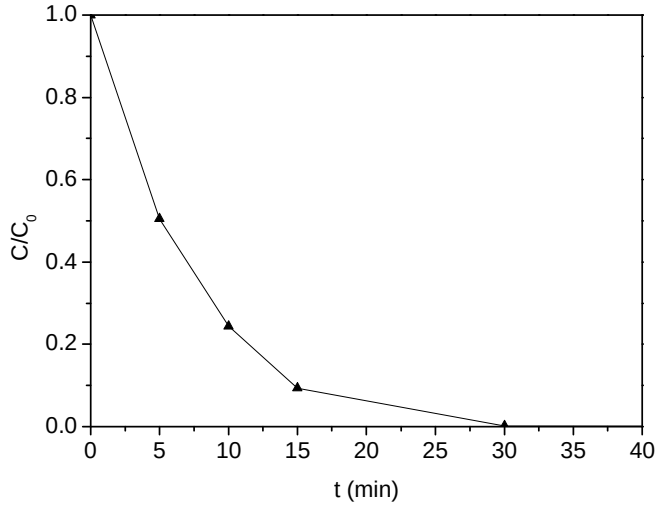


Figure 10.7 Evolution of dimensionless concentration of RB5 during non-catalytic ozonation (C_0 = 300 mg/L, pHi = 5.3).

With the increase in the concentration of the reactive dye from 50 to 300 mg/L, the time required for nearly complete mineralisation increased from 10 to ca. 30 minutes (cf. Figure 10.2). The experimental curves corresponding to the removal of TOC during non-catalytic and catalytic ozonation of the 300 mg/L RB5 solution are depicted in Figure 10.8. As expected, as the initial dye concentration increased, the extent of mineralisation of the RB5 solution decreased (Figure 10.6).

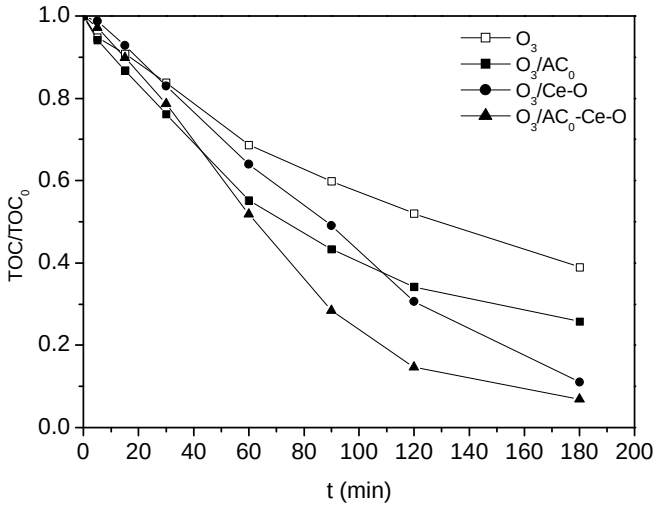


Figure 10.8 Evolution of dimensionless TOC during non-catalytic and catalytic ozonation of RB5 (C_0 = 300 mg/L, pHi = 5.6).

After 15 min of single ozonation 91% of initial colour was removed, although total decolourisation was only achieved after approximately 30 minutes of ozonation. Nonetheless, after this period of ozonation, only 16% of the TOC was removed. Cerium oxide had no visible activity up to this point of the reaction. Additionally, no major differences were observed between the performance of AC_0 and AC_0-Ce-O during this period. A distinct effect in the catalysts activity was more pronounced after the total decolourisation period. According to Figure 10.8, after 120 min of reaction, the activated carbon promoted ozonation increased TOC removal from 48% (obtained with non-catalytic ozonation) to 66%. Cerium oxide allowed a TOC removal of 69% and, for longer reaction times, better results were obtained comparatively to the performance of activated carbon alone. Similarly to what had been observed for the experiments with the lower dye concentration, the highest mineralisation degree was obtained with the AC_0-Ce-O composite. After an initial period, where the composite behaves likewise the activated carbon, the ozonation catalysed by the composite leads to an enhanced mineralisation extent, which is mostly due to the formation of $HO^{\bullet}$ radicals that are responsible for the mineralisation of the oxidation products. In fact, this period is coincident with that observed when comparing non-catalytic ozonation and ozonation catalysed by Ce-

O, where a significant catalytic effect starts to be observed after 30 min of reaction. A mineralisation degree of 85% is achieved after 120 min of reaction with AC_0-Ce-O, which is 1.8 times the value obtained with non-catalytic ozonation. Even though there is no experimental data concerning the concentration of dissolved ozone, it is believed that, in an early stage of the reaction, ozone is mainly consumed in the destruction of the chromophores of the dye molecules, and in the degradation of aromatic moieties and unsaturated compounds. As the refractory character of the solution increases, ozone is transformed into $HO^{\bullet}$ radicals that are responsible for the mineralisation of most of the compounds in solution. Simultaneously, oxidation of some of those products occurs on the surface of the activated carbon through a mechanism that involves, not only $HO^{\bullet}$ radicals, but also surface oxygenated radicals resultant from the reaction between ozone and activated carbon [23, 31].

Some selected samples collected during the ozonation experiments were analyzed by HPLC in order to evaluate the nature of the intermediate compounds. Due to the complexity of the dye molecule and to the large number of possible oxidation by-products, the HPLC analysis was focussed on the samples collected at longer reaction times (60, 120, 180 minutes). The intermediates and final products of the dyes ozonation reaction depend on their chemical structure. According to the literature [32, 33], aromatic amines, phenols, quinones, hydroquinones, phtalic, muconic, fumaric, maleic acids, etc. have been identified among the oxidation by-products generated. However, all of these by-products are detected at the early stages of ozonation and disappear completely for longer reaction periods. On the other hand, sulfate ions, nitrate ions, nitrogen, oxalic, formic and acetic acids were identified as final accumulated products. In this work, the qualitative evaluation of the chromatograms allowed the identification of carboxylic acids (oxalic and oxamic acid), which are responsible for a fraction of the TOC in solution. Nitrates were also detected in small concentrations. Sample AC_0-Ce-O led to nearly total mineralisation of the oxalic acid. Oxamic acid was produced in much lower concentrations than oxalic acid. Due to its extreme refractory character [23, 34] it was only partially removed from solution, being the lowest concentration detected for the O_3/AC_0 system. The concentration of nitrates was lower whenever either AC_0 or AC_0-Ce-O was used. These observations are in agreement with our previous findings related to the catalytic ozonation of several aromatic compounds and carboxylic acids [23, 35] (see chapters 5 and 6).

10.3.3 Effect of the presence of carbonates and bicarbonates in the ozonation of RB5

Generally, in addition to dyes, reactive dye baths involve the use of several auxiliary chemicals, such as sodium chloride (NaCl), sodium carbonate (Na_2CO_3), also known as soda ash, and sequestering agents. In this section, the influence of the addition of Na_2CO_3 in the catalytic ozonation of dye solutions is assessed. The main role of the Na_2CO_3 is to increase and buffer the pH of the dye bath, favouring the reaction between the reactive group of the dye and the -OH groups of the cellulose.

The presence of inorganic ions such as carbonates and bicarbonates may affect the destruction of organic compounds in water and wastewater through advanced oxidation processes. Carbonate (CO_3^{2-}) and bicarbonate ions (HCO_3^-) are well known as hydroxyl radical scavengers. Both species react with hydroxyl radicals to produce carbonate radical ions via the following reactions [36], respectively at moderate and high pH levels:

$$HCO_3^- + HO^\bullet \rightarrow CO_3^{-\bullet} + H_2O \qquad k = 8.5 \times 10^6\ M^{-1}\ s^{-1} \qquad (10.1)$$

$$CO_3^{2-} + HO^\bullet \rightarrow CO_3^{-\bullet} + HO^- \qquad k = 3.9 \times 10^8\ M^{-1}\ s^{-1} \qquad (10.2)$$

As demonstrated by the rate constants, carbonate ions are much stronger scavengers than bicarbonate ions. Therefore, in relation to the subject under discussion, the bicarbonate concentration eventually present in an ozone wastewater treatment process is less important than the concentration of carbonate.

The characterization of a textile effluent representative of a global effluent collected after a conventional activated sludge biological treatment, revealed a concentration of inorganic carbon (IC) of ca. 100 mgC/L, which is due to the presence of HCO_3^- and CO_3^{2-}.

Assuming that this content results mainly from the addition of Na_2CO_3 during the dyeing step, a concentration of approximately 1 g/L was estimated and used in the simulated coloured effluent. The addition of 1 g/L of Na_2CO_3 to the 300 mg/L RB5 solution led to a significant pH increase from ca. 5.6 to 11.5, which corresponds to the typical pH of a reactive dyeing bath. However, in order to meet the conditions usually found in real textile effluents after biological treatment, the pH of the solution was adjusted to 8.5 by the addition of HCl solution. At this pH the equilibrium of the HCO_3^- and CO_3^{2-} species is shifted towards the formation of HCO_3^-, as only ca. 1% of the acid is deprotonated (pKa [HCO_3^-/ CO_3^{2-}] = 10.4).

The simulated effluent was treated by catalytic and non-catalytic ozonation. Both colour and TOC removal were measured along time. With the exception of the system O_3/AC_0, which allowed a slightly faster colour removal, the decolourisation of the CI RB5 solution was not significantly enhanced during the catalytic ozonation (see Appendix G). Apparently, the rate of decolourisation seems to be slightly higher in this case, comparatively to the results obtained in the absence of carbonate species, which may be related to the solution pH (8.5 vs 5.3). After 15 min of reaction, the colour removal lies between 97% and 98% for all the catalytic systems and the time required for nearly total decolourisation was less than 30 minutes. The effect of the addition of sodium carbonate was mostly noticeable in the extent of the mineralisation of the solution. Experimental data referring to the TOC removal in all the studied systems is depicted in Figure 10.9.

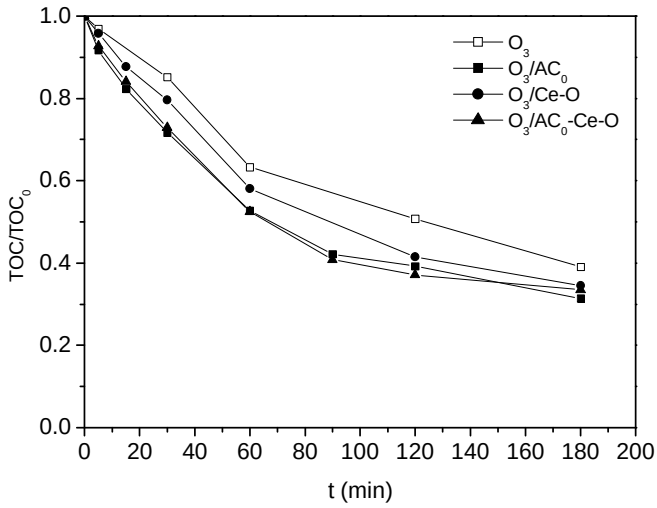


Figure 10.9 Effect of the presence of HCO_3^-/ CO_3^{2-} in the mineralisation of RB5 (C_0 = 300 mg/L, pHi = 8.5).

The results obtained by single ozonation are not significantly affected by the presence of HCO_3^-/ CO_3^{2-} (cf. Figure 10.8). Additionally, the catalytic action of AC_0 is only slightly affected, if compared with the results obtained in the absence of Na_2CO_3. On the contrary, those anionic species were found to strongly inhibit the

activity of both Ce-O and AC_0-Ce-O. As previously mentioned, the addition of Na_2CO_3 increases the solution pH and alkalinity. The mineralisation of organic compounds, achieved by ozonation, is usually favoured at higher pH values, due to the participation of $HO^{\bullet}$ radicals in the reaction mechanism. However, the scavenging effect of both of HCO_3^- and CO_3^{2-} species decrease the amount of $HO^{\bullet}$ radicals available for reaction with the organic compounds, therefore inhibiting the mineralisation process. In a previous work [25] (see chapter 8), cerium oxide was shown to catalyse the ozonation of carboxylic acids manly through the reactions involving $HO^{\bullet}$ radicals. In this work, the inhibiting effect of the HCO_3^-/ CO_3^{2-} confirms that the mineralisation of the intermediates of the process also occurs through a radical mediated reaction mechanism. Nevertheless, Ce-O still has a significant catalytic activity, as higher mineralisation is attained when compared to single ozonation. In the case of the composite, the results obtained up to 60 minutes of reaction are not affected by the presence of the sodium carbonate (compare Figure 10.8 and Figure 10.9). After this period, a significant reduction in the catalyst activity was observed. The removal of TOC obtained after 120 min of reaction was 63% contrasting with the 85% obtained in the absence of carbonates.

The similarity of the performance of AC_0 and AC_0-Ce-O in the mineralisation of the CI RB5 should be pointed out. Apparently, the presence of the scavenger has very little effect on the activity of the activated carbon, since only a slight reduction in the removal of TOC was observed for longer reaction period comparatively to the results obtained in the absence of the carbonates. This observation suggests that the contribution to the production of $HO^{\bullet}$ radicals is not the only role of activated carbon. It is thought that activated carbon also promotes the decomposition of dissolved ozone that may originate surface oxygen-containing radical species, which participate in the oxidation of the organic compounds. In this way, activated carbon seems to be a good catalyst for practical purposes, as its activity is not significantly affected by the presence of $HO^{\bullet}$ scavenging species.

10.3.4 Case study: catalytic ozonation applied to the treatment of textile effluents

Catalytic ozonation is a powerful chemical oxidation process that can be applied to the treatment of a vast range of organic pollutants, and it has been shown to be a promising technique to the treatment of wastewater from the textile industry. Due to

its high decolourisation efficiency and extensive elimination of organic content, catalytic ozonation can be used as a final refining treatment in order to allow an eventual reutilisation of water.

In order to evaluated the efficiency of the selected catalysts in the ozonation of real wastewater samples, liquid effluents originated in textile plants were assessed. In this context, a mixed textile effluent collected after biological treatment (TEA) and a raw textile wastewater (TEB) were used as case studies. Some characterization parameters are listed in Table 10.2.

Table 10.2 Parameters of the industrial textile effluents selected.

	Textile Effluent	
	Effluent A (TEA)	Effluent B (TEB)
origin	Mixed with domestic sewage and collected after bio-treatment	Raw effluent
pH	8.3	9.3
TOC (mgC/L)	27	150
IC (mgC/L)	108	57
Conductivity (mS/cm)	2.84	3.11
Colour	Reddish-brown	Strong blue
Abs (436 nm)*	0.186	0.307
Abs (525 nm)*	0.160	0.230
Abs (620 nm)*	0.084	0.282

* λ defined by ISO7887:1994 for the determination of colour in real samples.

Textile Effluent A (TEA) was collected in a collective wastewater plant, after conventional activated sludge treatment, but before the subsequent physico-chemical step. It is a mixture of effluents from different textile plants and includes a fraction of domestic wastewater. Therefore it is representative of a global bio-treated textile wastewater. This sample presented a strong red colouration and very few suspended solids. The UV-Vis spectrum of the effluent is depicted in Figure 10.10. The effluent was filtrated under vacuum before use.

Experiments of non-catalytic ozonation and ozonation catalysed by AC_0, Ce-O and AC_0-Ce-O were carried out under the same condition used for the synthetic coloured solutions. Despite the strong visible colour of the effluent, complete decolourisation was achieved by single ozonation in shortly after 5 minutes (Figure 10.10), confirming the strong decolourisation potential of ozone. In terms of colour removal, no significant improvement is obtained with catalytic ozonation (see Appendix G).

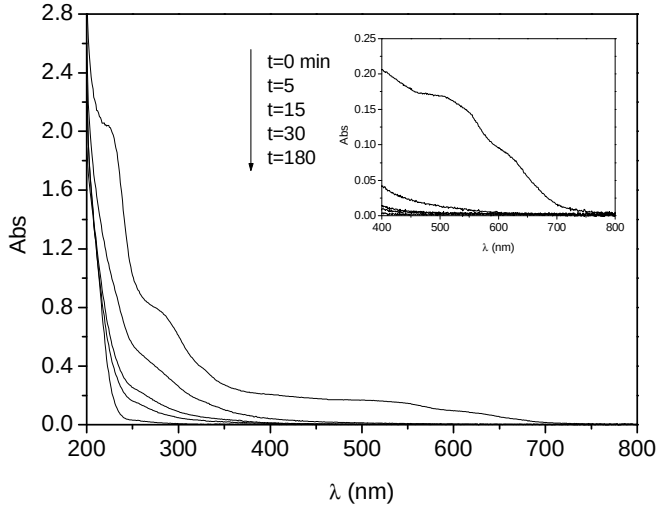


Figure 10.10 Evolution of the UV-Vis spectrum of TEA during non-catalytic ozonation (inset: magnification of the visible region of the spectrum).

Nevertheless, the mineralisation of the solution was negligible after 5 min of ozonation (less than 4% of TOC removal), bearing out that the decolourisation is not directly related to mineralisation extent. The evolution in the mineralisation degree of the effluent, achieved by the different catalytic systems is depicted in Figure 10.11, and compared to that obtained with non-catalytic ozonation.

Under the selected experimental conditions the effluent seems to be easily mineralised by non-catalytic ozonation, with a TOC removal of 75% being achieved after 120 min.

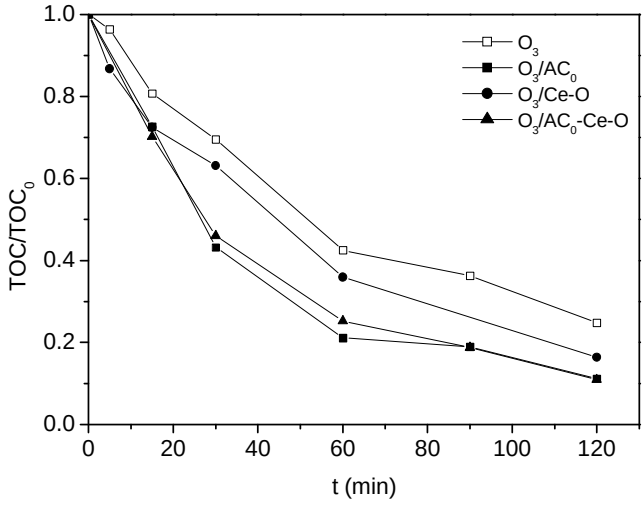


Figure 10.11 Evolution of dimensionless TOC during non-catalytic and catalytic ozonation of TEA.

Nonetheless, a higher mineralisation degree was achieved with catalytic ozonation, being AC_0 and AC_0-Ce-O the catalysts leading to the best results. In the presence of activated carbon, the removal of TOC achieved after 30 min was approximately 57%, which is significantly higher when compared to the 30% TOC removal achieved in non-catalytic ozonation. Unlike what was observed for all the studied dye solutions, no major differences were observed between activated carbon and the composite. Additionally, sample Ce-O was visibly less active. The performance observed during the catalytic ozonation of the bio-treated effluent was attributed to the presence of HCO_3^- and CO_3^{2-}, which, as explained in the previous section, act as radical scavengers, therefore inhibiting the mineralisation of the organic compounds via $HO^{\bullet}$ oxidation. AC_0 and AC_0-Ce-O have similar catalytic activities, which may be explained by the contribution of the surface reactions that are believed to occur preferentially on the activated carbon, therefore not involving $HO^{\bullet}$ radicals in solution.

Textile Effluent B (TEB) is a raw effluent collected in the equalisation tank of a wastewater treatment plant of a textile dyeing mill. Consequently, this wastewater is strongly coloured, and presents a relatively high organic load. Other

characterization parameters are summarised in Table 10.2. Due to the presence of suspended solids, the effluent was filtrated under vacuum before ozonation experiments. Following the same approach of the rest of this work, effluent TEB was ozonised in the presence of AC_0, Ce-O and AC_0-Ce-O, and the results were compared to those obtained with non-catalytic ozonation.

According to Figure 10.12, the ozonation time required for nearly total decolourisation is approximately 30 min.

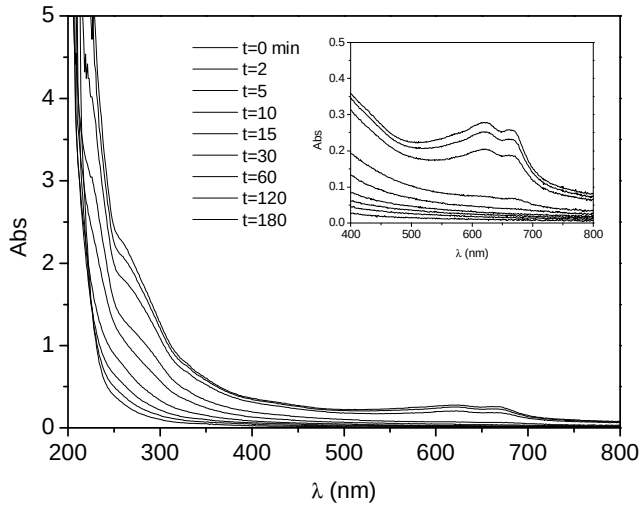


Figure 10.12 Evolution of the UV-Vis spectrum of TEB during non-catalytic ozonation (inset: magnification of the visible region of the spectrum).

In real water matrixes, the colour should be measured at three different wavelengths (436, 525 and 620 nm), according to what is established by ISO7887:1994. Analyzing the absorbance values along time obtained during non-catalytic and catalytic ozonation, is seems that the decolourisation of this effluent is slightly enhanced by the latter (see Appendix G).

Due to the high organic content of this effluent, the degree of mineralisation attained with single ozonation is quite low. Despite the effective decolourisation obtained, the TOC removal achieved after 30 min of ozonation was approximately only 6%. Longer reaction times lead to higher mineralisation levels. However, after

180 min of ozonation only 44% of the organic content was removed, as shown in Figure 10.13.

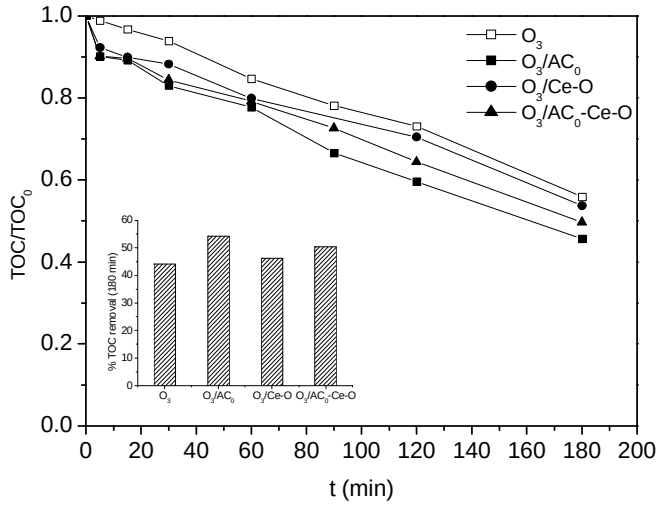


Figure 10.13 Evolution of dimensionless TOC during non-catalytic and catalytic ozonation of TEB (inset: % TOC removal achieved after 180min).

All the tested catalysts led to higher mineralisation levels, when compared to single ozonation. In this case, after 180 min of reaction best results were achieved with activated carbon, which allowed a TOC removal of 54%. Observing the experimental curves, and considering the amount or organic matter still present in solution after 180 min, it seems that, even longer reaction times, and consequently, higher ozone doses would be necessary to accomplish total mineralisation. When comparing the concentration of ozone in the gas phase at the outlet of the reactor, it is obvious that the consumption of ozone was much higher for TEB, comparatively to TEA, which is related to the nature and the concentration of the dissolved organic compounds.

According to the literature [3], and to the present results, ozonation is not suitable to be used as a main wastewater treatment. Conversely, the application of ozone processes as post-treatment for a refined depuration of wastewater is of great interest. In the case of liquid effluents from the textile industry, ozone has proven to be highly effective for an extensive elimination of colour. Concerning the removal

of recalcitrant compounds, which cannot be eliminated in biological processes, catalytic ozonation emerges a feasible solution to significantly enhance the mineralisation of such effluents.

10.4 Conclusions

The present study reports experimental kinetic data on the colour removal and mineralisation of CI Acid Blue 113, CI Reactive Yellow 3 and CI Reactive Blue 5 solutions, and two different textile effluents. Ozonation is a powerful oxidation process for fast and total decolourisation of both synthetic dye solutions and real textile effluents. Catalytic ozonation notably enhanced the mineralisation of the dye solutions. However, no major improvements were observed in the rates of colour removal. Such results are explained by the high decolourisation potential of ozone.

Within the experimental conditions settled for this work, adsorption in activated carbon was not efficient enough for the decolourisation of the dye solutions. The combination of activated carbon with ozone enhanced the mineralisation levels of both the dye solutions and the textile effluents.

The results obtained in this study show that cerium oxide catalysts is an effective ozonation catalyst for the mineralisation of textile dyes. Comparatively to the performance of the commercial activated carbon, an enhanced mineralisation extent was achieved, which is explained by a higher ability to catalyse the decomposition of ozone into $HO^{\bullet}$ radicals. A strong synergic effect was observed between activated carbon and cerium oxide in the prepared composite, leading to enhanced mineralisation degrees for all the studied dye solutions.

The mechanism of the ozonation catalysed by the ceria-activated carbon composite is believed to comprise both surface reactions, similar to what occurs with activated carbon promoted ozonation, and also liquid bulk reactions involving $HO^{\bullet}$ radicals, resultant from the catalytic decomposition of ozone on the surface of the catalyst, mainly in the presence of cerium oxide.

The presence of bicarbonate and carbonate ions in solution was shown to partially inhibit the mineralisation of the CI Reactive Blue 5 dye. The negative impact on both Ce-O and AC_0-Ce-O activities is supposed to be related to the scavenging effect of those inorganic ions on the $HO^{\bullet}$ radicals formed. The presence of high concentrations of inorganic ions with scavenging properties may restrain the results

obtained in wastewater treatment by advanced oxidation processes. Activated carbon catalysts also promote surface oxidation reactions that do not involve $HO^{\bullet}$ radicals in solution; therefore their activity is not severely affected by the presence of scavenger species. This was confirmed by testing the efficiency of these catalytic systems in the mineralisation of real textile effluents. Ozonation processes are not suitable to be used as main wastewater treatments. However, they are attractive alternatives to conventional physical-chemical processes, as tertiary treatments for bio-treated effluents.

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Part VI

Conclusions and Forthcoming Work

In this final part of the thesis, a general overview of the main results is presented, along with the most relevant conclusions. In the last chapter some ideas for forthcoming work are suggested.

11 General Overview and Concluding Remarks

Effluents from the textile industry containing dyestuffs and other persistent chemical products require adequate treatment before discharge. Among the vast array of existent wastewater treatment techniques, none has emerged as a simple, cost-effective and universally applicable method to the treatment of such effluents. Biological processes are by far the most attractive processes to be used as main treatment. However, post-treatment stages are commonly required to accomplish total colour removal and elimination of refractory compounds. From an environmental point of view, oxidative rather than separation methods should preferably be used for the refining treatment of textile wastewater.

Powerful oxidising methods, such as conventional ozonation and ozone-based processes, are becoming increasingly important as a final treatment technology to improve colour removal and the elimination of persistent pollutants present in bio-treated effluents. Once dissolved in water, ozone can react with many organic compounds via two possible pathways: direct reaction of molecular ozone or indirect reaction by formation of secondary oxidants, especially free radical species. Nevertheless, the action of ozone is often limited to the partial oxidation of organic matter, resulting in limited TOC and COD removals.

Catalytic ozonation is considered an emerging powerful technology for the elimination of persistent organic compounds. The benefits provided by the use of ozone-based heterogeneous catalytic systems have been demonstrated for the removal of several organic pollutants and for the treatment of different industrial wastewaters. From a practical application point of view, the integration of such processes with aerobic or anaerobic biological treatment processes would be of great interest for a thorough treatment of liquid effluents, such as those from the textile industry.

The ultimate goal of this PhD work was the study of catalytic ozonation processes for the tertiary treatment of textile effluents, in order to achieve extensive colour and enhanced mineralisation rates. Based on preliminary results obtained previously in my Master thesis, this work was manly focussed on the application of activated carbons with different surface chemical properties on the ozonation of several organic model compounds, as well as dyes and textile effluents. Additionally metal oxides and a composite of activated carbon and cerium oxide were also evaluated.

11.1 Ozone decomposition in the presence of activated carbon

The decomposition of ozone on the surface of activated carbon is thought to be one of the steps of the catalytic ozonation process. Within this scope, the first goal of the present work was the study of the decomposition of dissolved ozone in the presence of activated carbon, focussing on the influence of its textural and chemical properties.

Starting from the commercial activated carbon Norit GAC 1240 Plus (sample AC_0), two series of activated carbon samples, differing either in their surface chemistries or textural properties, were prepared, characterised and tested in the decomposition of ozone in the aqueous phase, at different pH values (3, 5, 7 and 9). The decay of the concentration of dissolved ozone is a function of the solution pH, and was visibly enhanced in the presence of activated carbon, regardless of its characteristics.

The rate of ozone decomposition was correlated with the chemical properties of the activated carbon. Among the three activated carbon samples with different acid-base properties (AC_0, ACH_2 and $ACHNO_3$), the more basic one (ACH_2) was found to lead to higher decomposition rates. Aqueous ozone decomposition in the presence of activated carbon results from the contribution of homogeneous reactions and heterogeneous reactions on the surface of the solid. The high π-electron density on the carbon basal planes, and the presence of groups with basic characteristics on the surface of the carbon has been suggested to be responsible for the instability of ozone in solution. Moreover, strong correlations between ozone decomposition and activated carbon textural properties were also found, confirming that activated carbons with higher surface areas favour the decomposition of ozone in solution.

It was observed that activated carbon exposure to dissolved ozone results in the oxidation of its external surface, which was confirmed by XPS analysis. On the other hand, no modification in the texture of the AC samples occurred. That oxidation of activated carbon samples resulted in a slight deactivation, as the rate of ozone decomposition decreased during some cycles of exposure to ozone. Nevertheless, they are still capable of promoting the decomposition of ozone. Even a highly acidic activated carbon sample with a large amount of oxygen surface functional groups is active for the decomposition of dissolved ozone.

11.2 Ozonation of organic model compounds catalysed by activated carbon and metal oxides

The second major part of the work was dedicated to the study of the catalytic ozonation of several organic compounds. Although the main goal was the treatment of textile effluents, simple organic molecules: aniline, sulfanilic acid (SA) and benzenesulfonic acid (BSA) were selected as model pollutants in order to better understand the catalytic ozonation process. The ozonation of such reactants leads to the formation of saturated compounds such as small chain carboxylic acids, which are usually highly refractory to conventional ozonation. In this work, oxalic acid was found to be a final ozonation product common to all the studied compounds. In the case of those containing nitrogen, oxamic acid was also identified. The catalytic ozonation of these two carboxylic compounds was also studied.

For comparative purposes, adsorption and non-catalytic ozonation were carried out under the same experimental conditions. The concentrations of the parent compounds as well as the formation of reaction intermediates were followed by HPLC. The determination of TOC was the analytical technique selected for the evaluation of the mineralisation, as well as for comparing the performance of the different catalytic systems.

The surface chemistry of the activated carbons influences the adsorption of aromatic compounds and those materials can be tailored to maximize their adsorption capacities. In a preliminary study on the adsorption of aniline, SA and BSA on activated carbon, it was concluded that, regardless of the nature of the adsorptive molecule, higher adsorption uptakes were achieved with sample AC_0 comparatively to sample $ACHNO_3$. Similar conclusions were withdrawn later, regarding the adsorption of carboxylic acids. Such higher affinity towards organic compounds may contribute to the enhanced results observed with this AC sample.

In order to clarify the activated carbon catalytic ozonation mechanism, and understand the influence of the surface chemical properties of this material on the ozonation process, additional experimental work was carried out with oxalic and oxamic acids. As the solution pH not only influences ozone decomposition in aqueous solutions, but also the surface properties of the catalyst and the dissociation of organic molecules in water, two level of pH were studied. The simultaneous use of ozone and activated carbon yields significant increases of oxalic and oxamic acid removal from water when compared to single ozonation and single adsorption,

proving the existence of a catalytic reaction mechanism. Exception was observed for oxamic acid, as it was found to be resistant to oxidation at neutral and basic pH. Generally, the presence of activated carbon during ozonation increased the rate of degradation of both carboxylic acids leading to enhanced mineralisation levels. Also in this case, a higher basicity of the activated carbon improved the efficiency of this process.

The low reactivity of oxamic and oxalic acids towards direct ozonation, and the limited influence of the $HO^{\bullet}$ radical scavenger *tert*-butanol, observed at pH 3, suggest that the oxidation occurs mainly through reactions on the surface of the activated carbon. In the case of oxalic acid at pH 7, the results can be explained by a mechanism involving both surface and bulk reactions between the organic solute and hydroxyl radicals, resultant from the decomposition of ozone. For both carboxylic acids, the efficiency of activated carbon promoted ozonation decreases with the increase of solution pH. At least in part, this might be related to the observed lower affinity towards activated carbon surface.

Activated carbon was found to enhance the mineralisation of aniline, SA and BSA. In all the cases, sample AC_0, which has basic characteristics comparatively to sample $ACHNO_3$, led to the best results, mainly in terms of mineralisation. Selected experiments carried out in the presence of a radical scavenger (*tert*-butanol), evidenced the participation of $HO^{\bullet}$ radicals in the oxidation mechanism in the degradation of benzenesulfonic acid, and in the mineralisation of the respective oxidation by-products. However, no significant similar effect was observed in the degradation of sulfanilic acid.

The removal of the studied aromatic compounds, as well as the respective oxidation by-products, via ozonation in the presence of activated carbon is a result of a complex combination of homogeneous and heterogeneous reactions. On one hand, both direct and indirect ozone reactions occur in the liquid phase. Additionally, reactions between adsorbed species and oxygen-containing radicals formed on the surface of the activated carbon are assumed to occur.

Regarding the non-catalytic decomposition of ozone in aqueous solution, it is established that it is initiated by the presence of HO^- ions; so pH plays a major role in this process:

$$O_3 \xrightarrow{HO^-} HO^{\bullet} \qquad (11.1)$$

It was observed that activated carbon accelerates the decomposition of ozone in aqueous phase. Both textural and surface chemical properties influence that decomposition, and two possible pathways can explain the decomposition of O_3 in the presence of activated carbon. The first one assumes that activated carbon acts as an initiator of the decomposition of ozone leading to the formation of free radical species, such as $HO^{\cdot}$, in solution:

$$O_3 \xrightarrow{AC} HO^{\bullet} \tag{11.2}$$

Another possibility is the adsorption and reaction of ozone molecules on the surface of the activated carbon, yielding surface oxygenated free radicals:

$$AC + O_3 \rightarrow AC - O \tag{11.3}$$

where AC-O stands for any oxygen-containing active species on the surface of the activated carbon, which can react with adsorbed organic species.

Aromatic compounds (Ar) with electron donor groups, such as -OH and -NH_2, have a high electronic density in *ortho-* and *para-* positions. Consequently, such aromatic compounds react actively in those positions with ozone by electrophilic attack. This results in the formation of several intermediates that are further transformed into saturated compounds (*I*), which cannot be mineralised by direct ozone attack. Additionally, $HO^{\cdot}$ radicals can also contribute to the oxidation of the aromatic compounds, which are more refractory towards molecular ozone attack, as seems to be the case of BSA. The mineralisation of the oxidation intermediates into CO_2 and inorganic ions (e.g. NO_3^-, NH_4^+, SO_4^{2-}), represented by *P*, occurs either in the liquid phase through $HO^{\cdot}$ radical attack, or on the surface of the activated carbon. Steps (11.4) to (11.8) schematically represent the proposed pathways.

$$Ar + O_3 \rightarrow I \tag{11.4}$$

$$Ar + HO^{\bullet} \rightarrow I \tag{11.5}$$

$$I + HO^{\bullet} \rightarrow P \tag{11.6}$$

$$AC + I \rightarrow AC - I \tag{11.7}$$

$$AC - I + AC - O \rightarrow P \tag{11.8}$$

Even though there is no experimental evidence, it is necessary to consider that adsorbed reactants might also react with dissolved ozone, or hydroxyl radicals from the aqueous phase.

$$AC + Ar \rightarrow AC - Ar \quad (11.9)$$

$$AC - Ar + O_3 \, or \, HO^{\bullet} \rightarrow I \quad (11.10)$$

It was shown that the presence of the radical scavenger *tert*-butanol induced different results depending on the aromatic compound studied. It inhibited the conversion of BSA, but no significant effect was observed for SA. However, in both cases the removal of oxidation by-products was influenced by the radical scavenger, which suggests the important role of the formation and reaction of $HO^{\bullet}$ radicals. This supplies experimental evidence for the occurrence of steps (11.5) and (11.6). The possibility of the existence of reactions occurring on the surface of activated carbon without the main involvement of $HO^{\bullet}$ radicals in solution was highlighted during the ozonation of oxalic and oxamic acids, especially at acid pH.

Another goal of this work was the development of metal oxide based catalysts for the application in ozonation reactions. Oxides of manganese (Mn), cobalt (Co), and cerium (Ce), as well as binary mixtures of (Ce-Mn) and (Ce-Co) were prepared and tested in the ozonation of aniline and sulfanilic acid. In this initial screening test, all the materials were found to improve the mineralisation of those model compounds. The experimental results showed that intimate mixtures of metal oxides of Ce-Mn and Ce-Co, obtained by co-precipitation, are slightly more efficient ozonation catalysts than the corresponding single metal oxides, which might be related both to their higher surface areas and enhanced redox properties.

Among the catalysts tested, cerium oxide was chosen for further studies and oxalic and oxamic acids were selected for a more detailed study. Ozonation experiments carried out at acid pH in the presence of *tert*-butanol, showed that cerium oxide catalyses the oxidation of those organic compounds mostly by the formation of $HO^{\bullet}$ radicals, which react with the organic compounds in solution. This was experimentally observed for both oxalic and oxamic acids. Nevertheless, the existence of an additional pathway involving the adsorption and reaction on the Ce-O should not be ruled out.

In order to combine the properties of activated carbon and ceria, and to search for possible synergies between them, a composite with approximately 50% wt of each material was prepared and characterised. According to the XPS results, the composite has a higher percentage of surface Ce(III) species, comparatively to the prepared CeO_2. Relatively to the activated carbon and to the single oxide, the composite was found to achieve better results. A significant synergic effect was

observed for the catalytic ozonation of oxalic acid. Similar results were obtained with the BSA. In both cases nearly complete mineralisation was achieved. In the case of aniline and SA also better results were obtained with the composite.

The reaction mechanism is believed to comprise both surface reactions, similar to what is believed to occur in activated carbon promoted ozonation, and also liquid bulk reactions involving $HO^{\cdot}$ radicals. It was assumed that the existence of delocalized electrons on the basal planes of the activated carbon contributes to the formation of Ce (III) species, which are thought to be necessary for promoting the decomposition of O_3 into $HO^{\cdot}$ radicals by redox reactions on the catalyst surface involving the pair Ce(III)/Ce(IV).

11.3 Application of catalytic ozonation to the treatment of textile dyes and effluents

The catalytic ozonation of three commercial textile dyes (CI Acid Blue 113, CI Reactive Yellow 3 and CI Reactive Blue 5) was carried out under the same experimental conditions. The results were compared to those obtained in non-catalytic ozonation and adsorption on AC_0. The influence of the presence of Na_2CO_3, which is an auxiliary chemical used in reactive dyebaths, was studied in the ozonation of CI Reactive Blue 5. Activated carbon (AC_0), cerium oxide (Ce-O) and the ceria-activated carbon composite were the catalysts selected for this part of the work. Generally, catalytic ozonation notably enhanced the mineralisation of the dye solutions. However, no major improvements were observed in the rates of colour removal, which was explained by the high decolourisation potential of ozone. Within the experimental conditions settled for this work, adsorption in activated carbon was not efficient enough for the decolourisation of the dye solutions. The combination of activated carbon with ozone enhanced the mineralisation levels of both the dye solutions and the textile effluents. The results obtained in this study show that cerium oxide is an effective ozonation catalyst for the mineralisation of textile dyes. Comparatively to the performance of the commercial activated carbon, an enhanced mineralisation extent was achieved with the composite, which is explained by a higher ability to catalyse the decomposition of ozone into $HO^{\cdot}$ radicals.

The presence of bicarbonate (HCO_3^-) and/or carbonate ions (CO_3^{2-}) in solution was shown to partially inhibit the mineralisation of the CI Reactive Blue 5 dye. The negative impact on both Ce-O and AC_0-Ce-O activities is supposed to be related to the scavenging effect of those inorganic ions on the $HO^{\bullet}$ radicals. The presence of high concentrations of inorganic ions with scavenging properties may restrain the results obtained in wastewater treatment by advanced oxidation processes. However, activated carbon catalysts also promote surface oxidation reactions that do not involve $HO^{\bullet}$ radicals in solution; therefore their activity is not significantly affected by the presence of scavenger species.

Finally, the mentioned catalytic systems were tested in the degradation of real wastewater generated in the textile industry. A raw wastewater resultant from a dyeing mill and a representative effluent collected in a wastewater plant immediately after conventional activated sludge treatment were used as case studies. Ozonation processes are not suitable to be used as main wastewater treatments. However, they are attractive alternatives to conventional physical-chemical processes as tertiary treatments. Particularly in the case of the bio-treated effluent, catalytic ozonation was found to enhance the mineralisation degree achieved. Among the catalysts tested, activated carbon was found to be promising as its activity is not significantly inhibited by the presence of inorganic species with scavenging effect, as is the case of HCO_3^-/CO_3^{2-}.

12 Suggestions for Forthcoming Work

There is still much work to be done regarding catalytic ozonation systems. The work presented in this thesis was mainly dedicated to the study of ozonation catalysed by activated carbons. Other carbon materials with tailored surface chemistry and textural properties are possible alternatives to be studied. This is the case of carbon xerogels or aerogels, and ordered mesoporous carbons obtained via the silica SBA-15 by the templating technique.

The good results achieved with the composite of ceria and activated carbon should be further explored, in order to optimize the preparation method, the material composition and study their stability in oxidation reactions in the aqueous phase. Other oxides (e.g. manganese or cobalt) and respective composites with activated carbon, as well as mixed oxides (e.g. CeO_2-ZrO_2) are also possible catalysts to be tested in ozonation reactions.

Regarding the scale-up, continuous experiments in column should be carried out. For that purpose, the preparation of catalysts supported on monolith structures would be of great interest.

In the present work the main focus was the tertiary treatment of effluents from the textile industry. Even tough this is still a matter that deserves the study for better solutions, other compounds normally present in industrial wastewater could also be the aim of catalytic ozonation. This technique is also promising in the scope of water treatment, particularly for the elimination of emergent organic pollutants (antibiotics, pesticides, hormones).

Appendices

Appendix A. Schematic representation of the experimental set-up

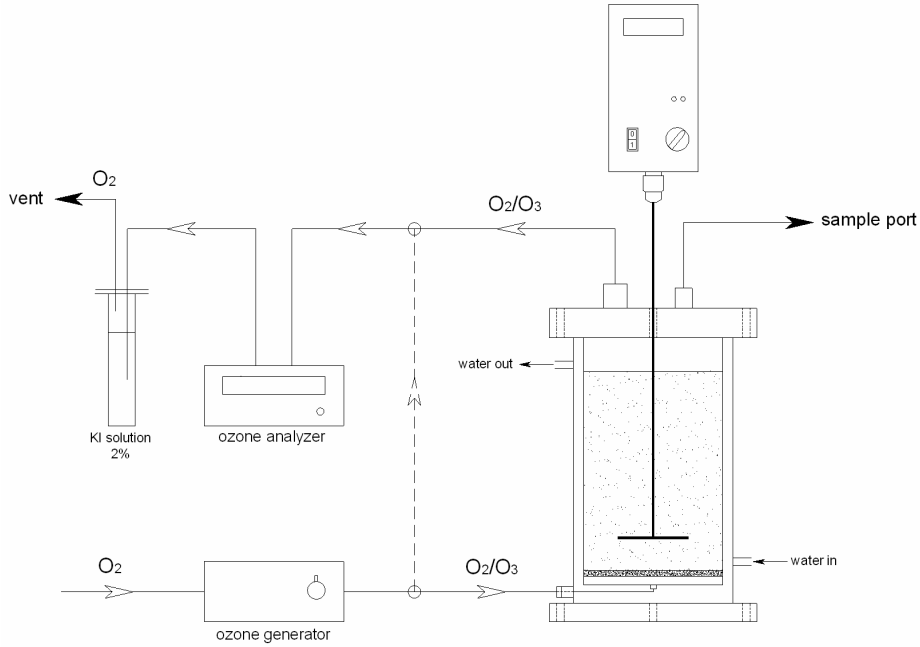


Figure A.1 Representation of the experimental set-up used for the adsorption and ozonation experiments.

Appendix B. Supporting information for chapter 2

Table B.1 Proximate analysis of the activated carbon samples.

Sample	Moisture (% wt)	Volatiles (% wt)	C_{fixed} (% wt)	Ash (% wt)
AC_0	3.24	2.67	88.50	5.58
ACH_2	1.17	2.03	90.76	6.03
$ACHNO_3$	4.49	11.43	79.85	4.23
ACN_2	1.20	1.82	91.46	5.52
ACg4h	1.24	1.83	88.86	8.06
ACg6h	0.89	2.54	86.18	10.39
ACg8h	1.15	1.97	85.79	11.10

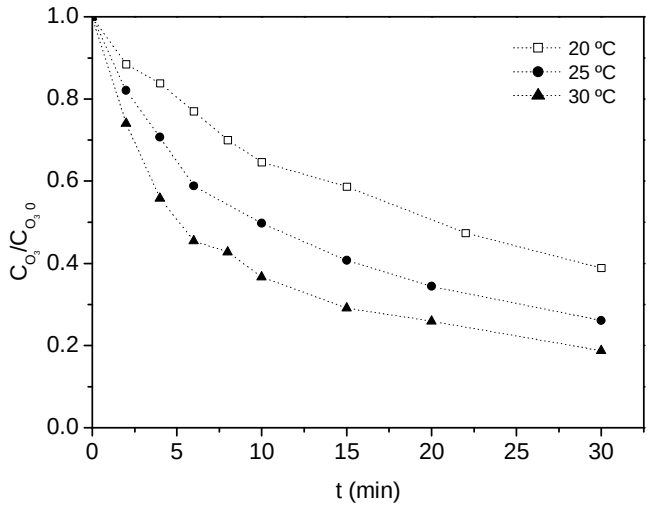


Figure B.1 Influence of the temperature of the solution on the homogeneous decomposition of dissolved ozone.

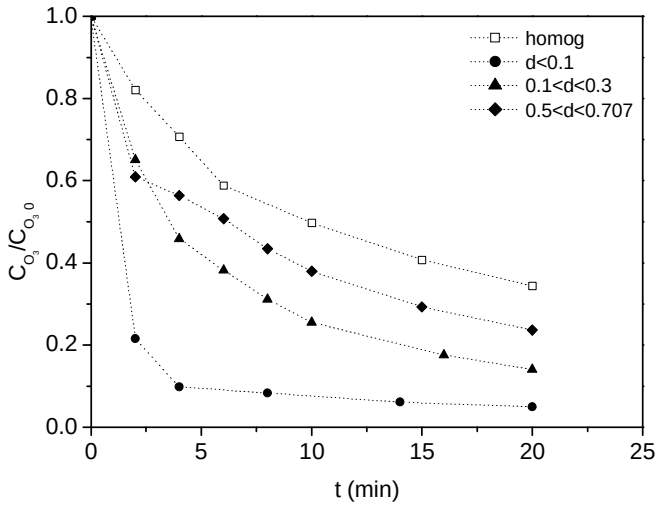


Figure B.2 Influence of the particle size (mm) of the activated carbon on the decomposition of dissolved ozone in the presence of AC_0 at pH 7.

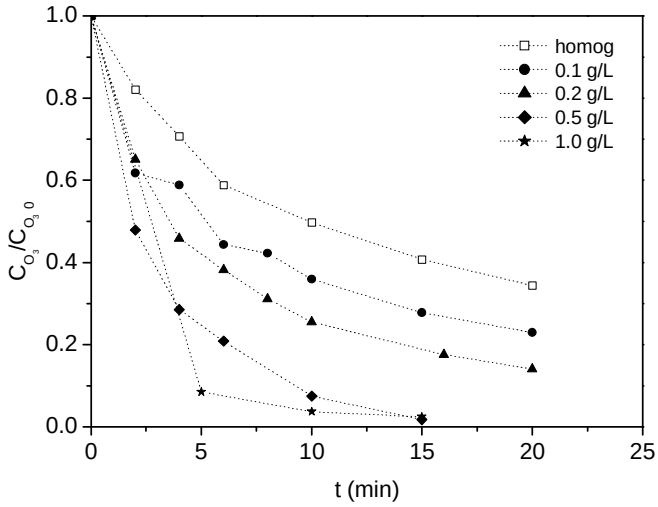


Figure B.3 Influence of the amount of activated carbon on the decomposition of dissolved ozone in the presence of AC_0 at pH 7.

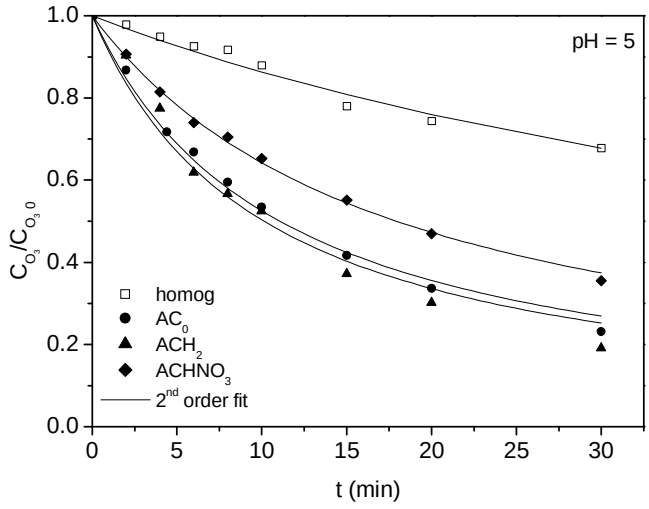


Figure B.4 Influence of AC surface chemistry on the heterogeneous decomposition of ozone at pH 5.

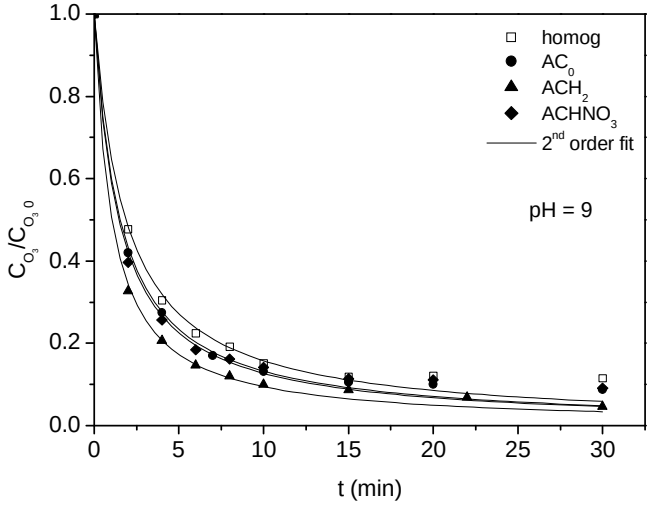


Figure B.5 Influence of AC surface chemistry on the heterogeneous decomposition of ozone at pH 9.

Appendix C. Supporting information for chapter 4

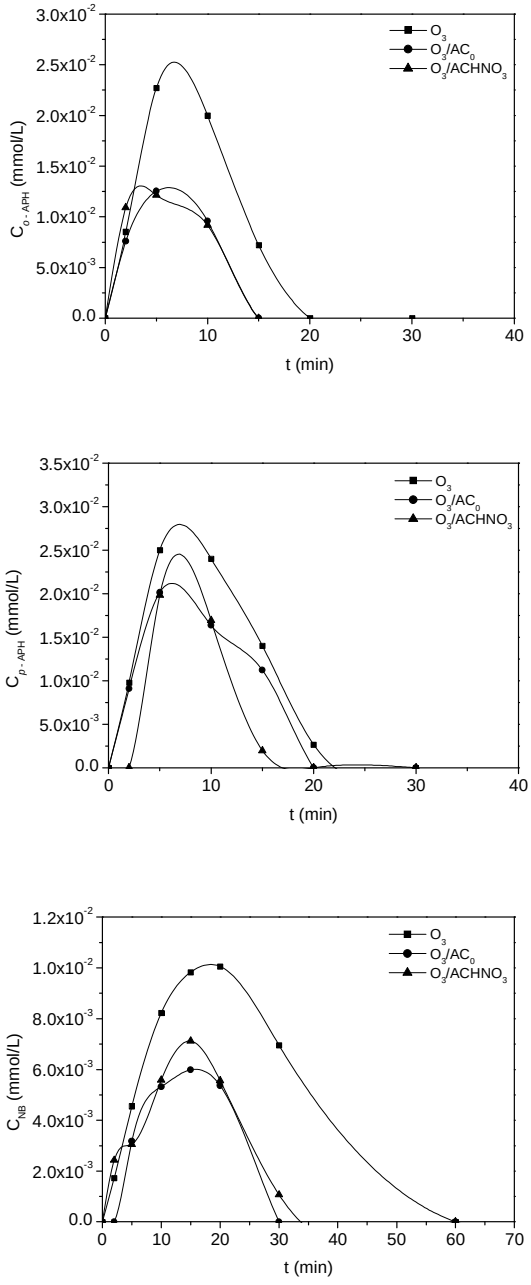


Figure C.1 Evolution of concentrations of o-aminophenol (*o*-APH), *p*-aminophenol (*p*-APH), and nitrobenzene (NB) during ozonation (■) and ozonation in the presence of AC_0 (●) and $ACHNO_3$ (▲) at pH 3.

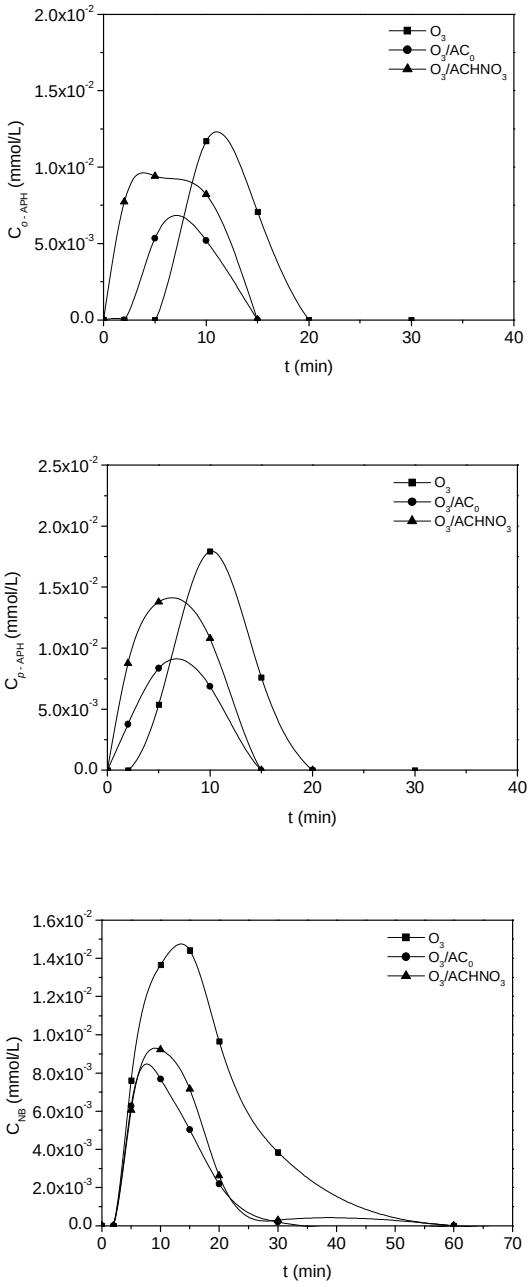


Figure C.2 Evolution of concentrations of o-aminophenol (*o*-APH), *p*-aminophenol (*p*-APH), and nitrobenzene (NB) during ozonation (■) and ozonation in the presence of AC_0 (●) and $ACHNO_3$ (▲) at pH 9.

Appendix D. Supporting Information for chapter 5

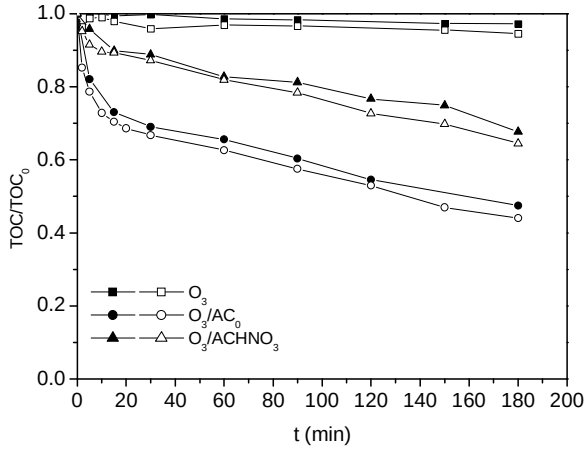


Figure D.1 Experimental TOC (filled symbols) versus TOC calculated from the residual concentration of oxamic acid in solution (open symbols) during non-catalytic and catalytic ozonation at pH 3 (C_0 = 1 mM, AC = 0.5 g/L).

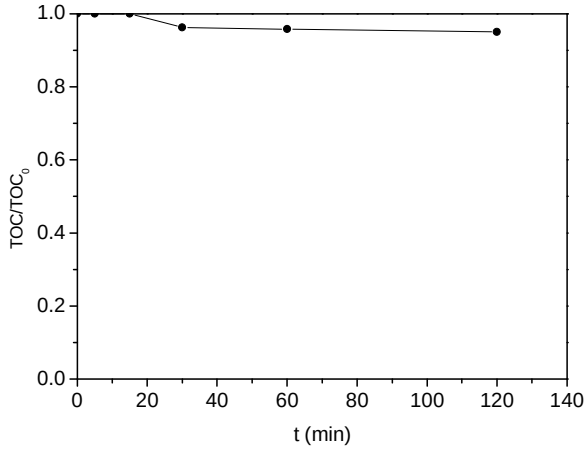


Figure D.2 Dimensionless TOC during ozonation of oxamic acid in the presence of AC_0, at pH 12 (C_0 = 1 mM, AC = 0.5 g/L).

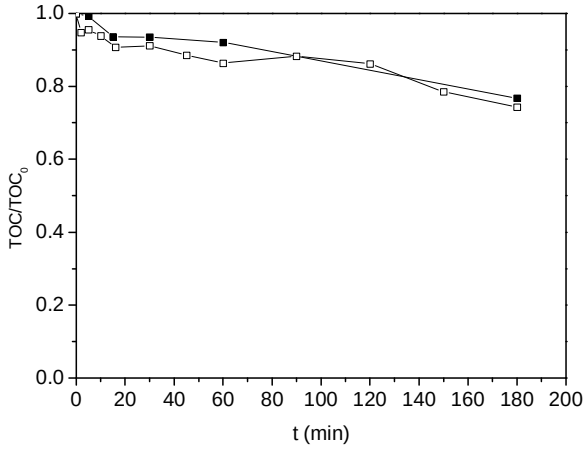


Figure D.3 Experimental TOC (filled symbols) versus TOC calculated from the residual concentration of oxalic acid in solution (open symbols) during non-catalytic ozonation at pH 3 (C_0 = 1 mM, AC = 0.5 g/L).

Appendix E. Supporting Information for chapter 7

The quantification of manganese and cobalt leached to solution during the ozonation of aniline at pH 6, in the presence of Mn-O, Co-O, Ce-Co-O and Ce-Mn-O, was accomplished by atomic absorption spectroscopy. The results obtained are depicted in the following figures.

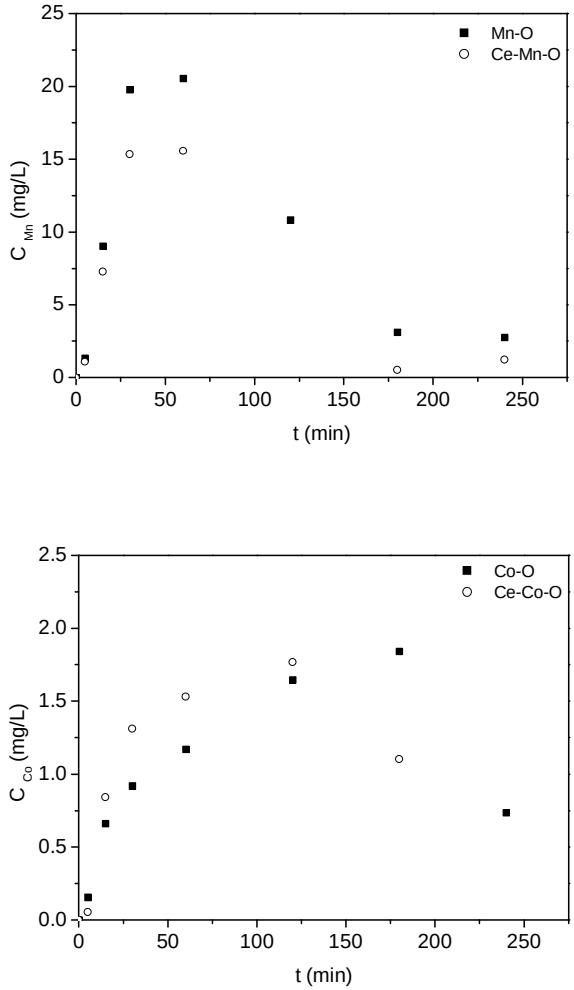


Figure E.1 Manganese and cobalt leaching to solution during the ozonation of aniline at pH 6.

Appendix F. Supporting Information for chapter 8

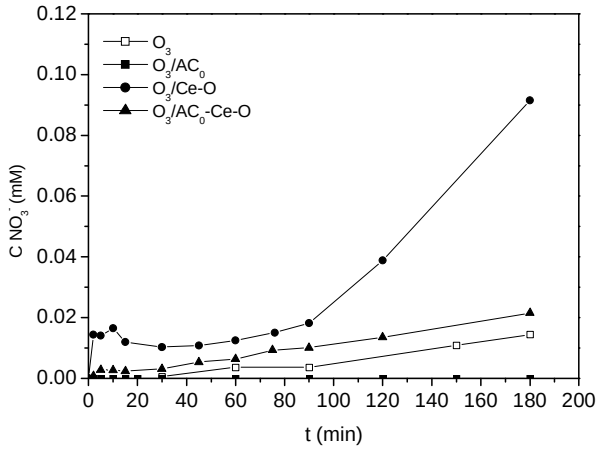


Figure F.1 Concentration of NO_3^- detected during non-catalytic and catalytic ozonation of oxamic acid at pH 3 (C_0 = 1 mM, catalyst = 0.5 g/L).

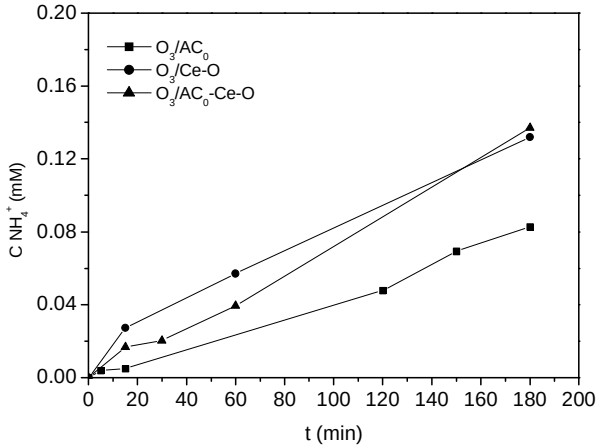
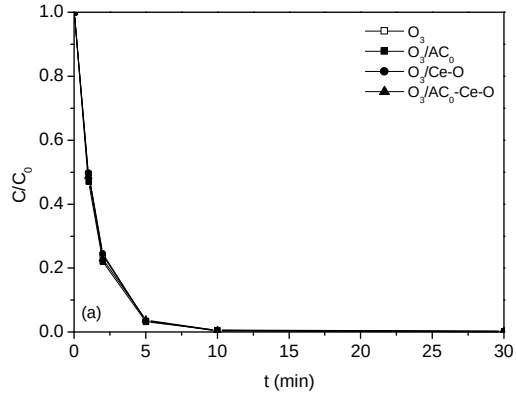
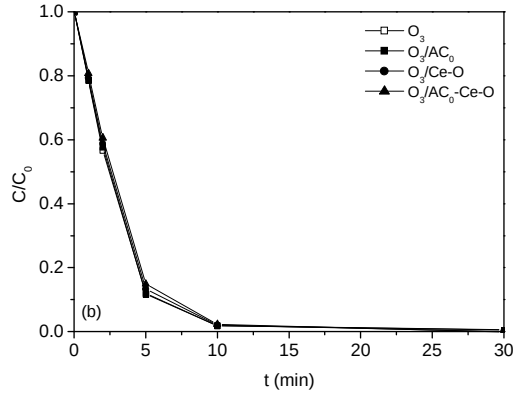


Figure F.2 Concentration of NH_4^+ detected during non-catalytic and catalytic ozonation of oxamic acid at pH 3 (C_0 = 1 mM, catalyst = 0.5 g/L).

Appendix G. Supporting information for chapter 10

Comparison of different catalytic systems in the decolourisation of CI AB113, CI RY3 and CI RB5 solutions with initial concentration of 50 mg/L. The concentration was measured at the wavelength corresponding to the maximum absorption in the visible region of the UV-Vis spectrum of each dye (Table 10.1).





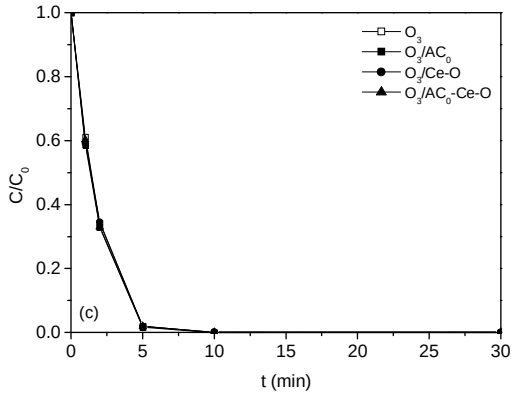


Figure G.1 Evolution of the dimensionless concentration of (a) AB113, (b) RY3 and (C) RB5 during non-catalytic and catalytic ozonation (C_0 = 50mg/L, natural pH).

Comparison of the extent of mineralisation obtained for the selected dyes with different catalytic systems.

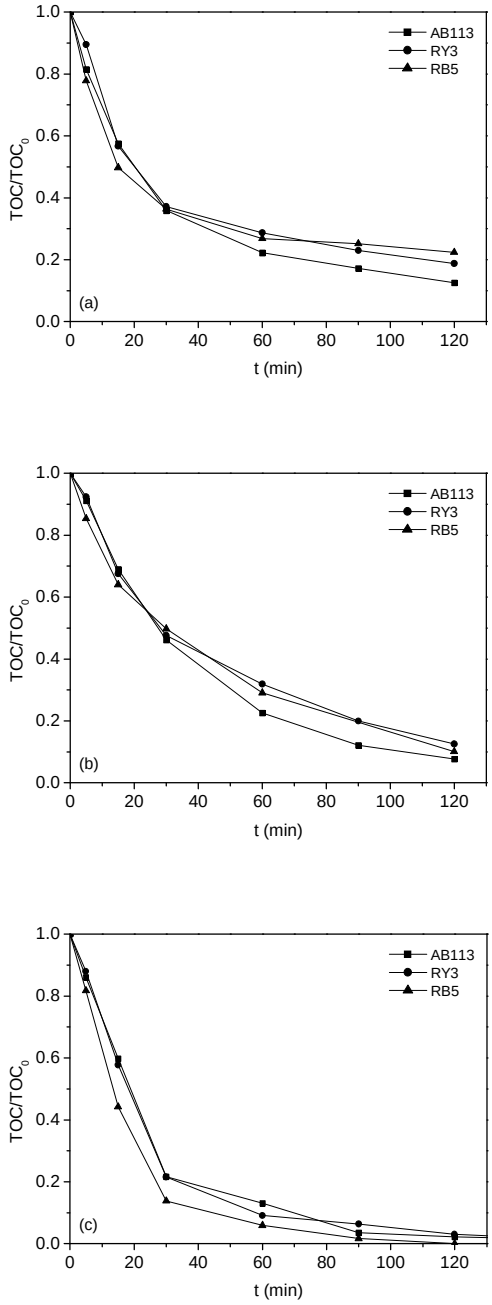


Figure G.2 Evolution of dimensionless TOC during ozonation of AB113, RY3 and RB5 catalysed by (a) AC_0, (b) Ce-O and (c) AC_0-Ce-O (C_0 = 50mg/L, natural pH).

Comparison of different catalytic systems in the decolourisation of solutions of CI RB5 with initial concentration of 300 mg/L, in the presence of Na_2CO_3.

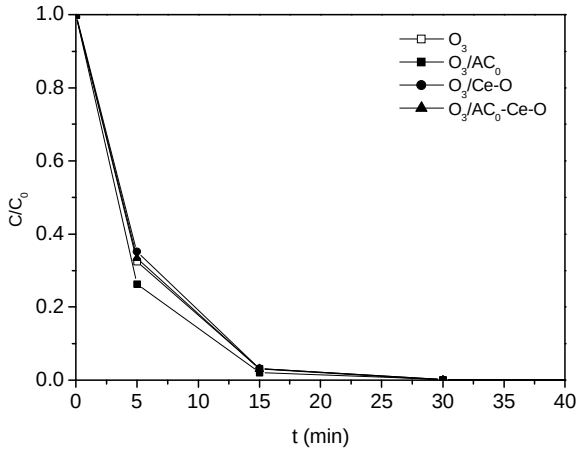


Figure G.3 Evolution of the dimensionless concentration of RB5 during non-catalytic and catalytic ozonation in the presence of Na_2CO_3 (C_0 = 300mg/L, pH = 8.5).

Decolourisation of sample TEA assessed at three wavelengths according to ISO7887:1994.

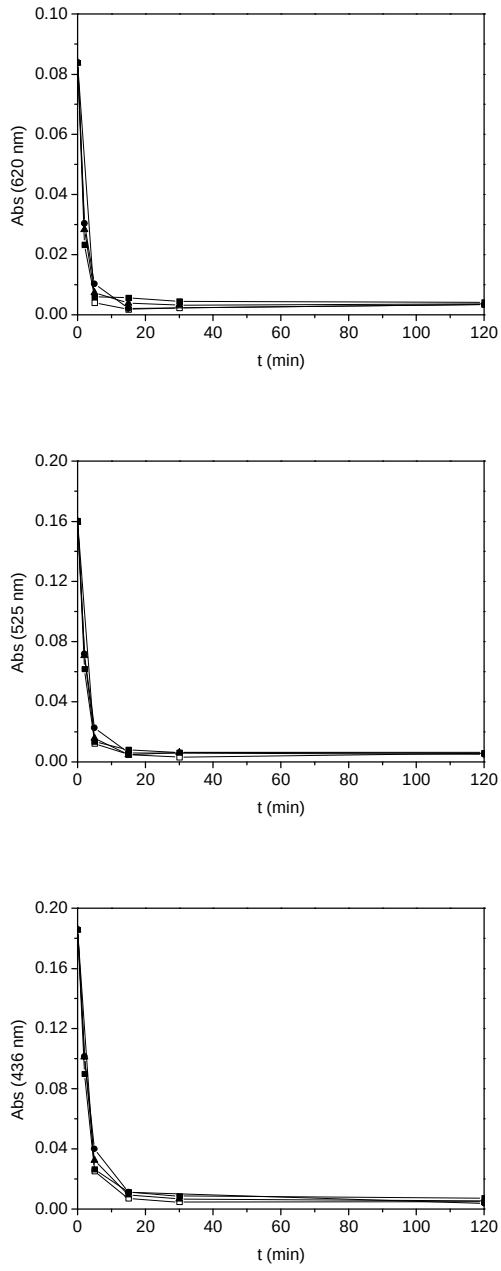


Figure G.4 Evolution of the absorbance of TEA, measured at 620, 525 and 436 nm, during non-catalytic ozonation (□), and ozonation catalysed by AC_0 (■), Ce-O (●) and AC_0-Ce-O (▲).

Decolourisation of sample TEB assessed at three wavelengths according to ISO7887:1994.

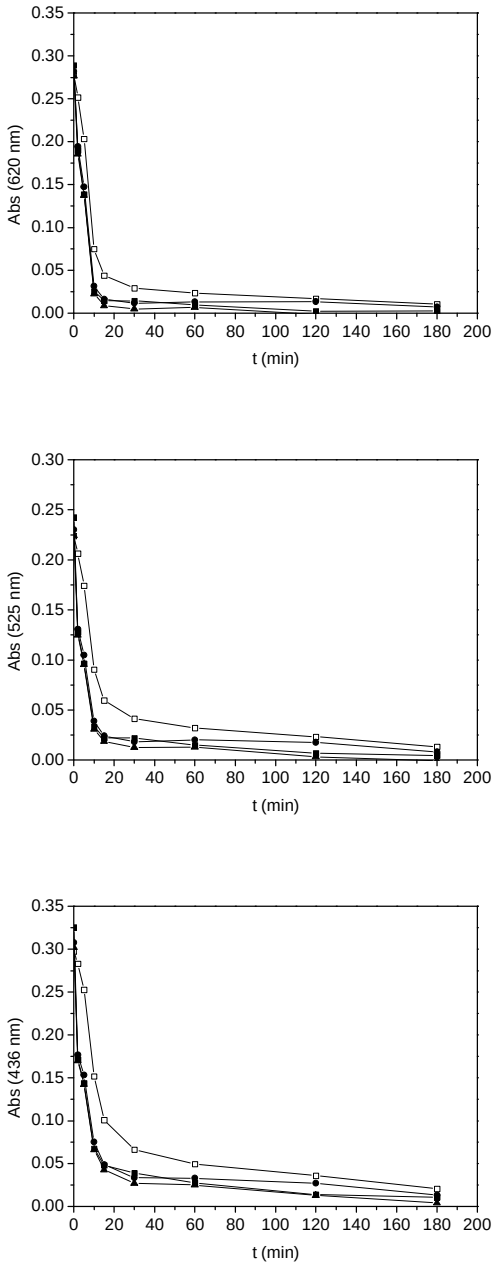


Figure G.5 Evolution of the absorbance of TEB, measured at 620, 525 and 436 nm, during non-catalytic ozonation (□), and ozonation catalysed by AC_0 (■), Ce-O (●) and AC_0-Ce-O (▲).